VOL. XXII. [MARCH, 1900.] NO. 3.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

## SUBSTITUTES FOR HYDROCHLORIC ACID IN TESTING CARBONATES.

BY JOSEPH W. RICHARDS AND NORMAN S. POWELL.

Received January 23, 1900.

THE following experiments were undertaken in the hope of finding a satisfactory substitute for hydrochloric acid in producing effervescence with natural carbonates. It is well-known that hydrochloric acid is difficult to carry in a portable set of apparatus, and while it is entirely satisfactory to use it in the laboratory, yet it would be very desirable to have some solid material to replace it in a portable testing outfit.

The materials tested as substitutes were potassium acid sulphate, citric acid, tartaric acid, and oxalic acid. These were made into solutions of the strength of 4 parts of water to 1 part of salt or acid, or 20 per cent. solutions. This would correspond roughly to dissolving a piece the size of a pea in 1 cc. of water. Such a solution, in a test-tube, makes a suitable reagent. Oxalic acid, however, requires about twice as much water as above given for complete solution. Therefore this was of about 10 per cent. strength.

The carbonates tested were as follows: calcite, dolomite, magnesite, siderite, rhodochrosite, smithsonite, aragonite, wither-

ite, strontianite, cerussite, barytocalcite, phosgenite, malachite, azurite, hydrozincite, lansfordite.

These were taken as representative of the common natural carbonates. Each mineral both as lump and powder was tested in cold, warm, and nearly boiling solutions of each reagent. For convenience in recording the results, the following numbers are used in the table to designate the degrees of effervescence.

0. No action.
1. Gas evolved in traces.
2. Gas evolved faintly, but plainly.
3. Gas evolved freely, not strongly.
4. Gas evolved strongly.
5. Gas evolved violently.

The results were, in general, that the powder was acted on more violently than the lump, and the action was stronger as the solution was warmer; but there were exceptions to these rules, which will be noted.

### POTASSIUM ACID SULPHATE.

(20 per cent. solution.)

*Cold:* Nearly half the carbonates were unacted on, or acted on only in traces. *Warm:* All were acted upon, but cerussite, strontianite and phosgenite only faintly, and witherite in traces. In these four cases, the insolubility of the sulphates of the bases present explains the faint action. *Hot:* All were acted upon, the majority strongly, but cerussite and phosgenite yet faintly, and witherite only in traces, as before. With careful observation, this test should positively detect any carbonate with the possible exception of witherite.

The action of this reagent on *calcite*, *dolomite*, and *magnesite*, is interesting. In lukewarm solutions the powders effervesce as follows: calcite strongly, dolomite freely but not strongly, and magnesite only faintly. This corresponds to their order with hydrochloric acid. But when a *lump* of each is put into *hot* solution, nearly boiling, the order is reversed: Calcite effervesces freely, dolomite strongly, and magnesite violently. The differences are very easily noted, and make this test quite practicable for distinguishing between these minerals. For distinguishing calcite from dolomite, the action of the cold solution on the

powder is also decisive : calcite powder effervesces strongly, at once ; dolomite powder only faintly.

### OXALIC ACID.

(10 per cent. solution.)

*Cold :* About half the carbonates were unacted upon. *Warm :* All were acted upon, but nearly half only faintly; only two strongly. *Hot :* All were acted upon, the majority freely, a few only faintly, only one violently. With ordinary care in observing, this test is satisfactory for all the carbonates tried.

With calcite, dolomite, and magnesite, the effervescence increased in the order given. In cold solution, calcite was unacted upon either in lump or powder ; dolomite showed traces of gas ; magnesite showed gas evolved plainly. In hot solution, calcite effervesced freely but not strongly, dolomite strongly, magnesite violently. The insolubility of calcium oxalate accounts, of course, for this behavior.

### CITRIC ACID.

(20 per cent. solution.)

*Cold :* About half the carbonates were unacted on, or acted on only in traces. *Warm :* All were acted on, about one-third faintly, one-third freely, and one-third strongly. *Hot :* All were acted upon, only three (phosgenite, rhodochrosite, and azurite), as low as freely, the rest being strongly to violently affected.

We recommend this reagent as entirely satisfactory, for testing either lump or powder in hot solution. This reagent also distinguishes clearly calcite from dolomite, for in cold solution calcite effervesces faintly to freely, and dolomite is entirely unacted upon.

### TARTARIC ACID.

(20 per cent. solution.)

*Cold :* Only three carbonates were unacted upon, smithsonite, rhodochrosite, and phosgenite; about half were acted on faintly, the rest freely, one strongly. *Warm :* All were acted upon, one-third faintly, one-third freely, one-third strongly. *Hot :* All acted upon, only rhodochrosite and phosgenite as low as *freely*

| | | Potassium Hydrosulphate. 20 % solution. | | | Citric Acid. 20 % solution. | | | Tartaric Acid. 20 % solution. | | | Oxalic Acid. 10 % sol. with excess of undissolved acid. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cold | Warm | Hot | Cold | Warm | Hot | Cold | Warm | Hot | Cold | Warm | Hot |
| Calcite ..... | Lump | 1 then stops | 2 | 3 | 1–2 | 3½ | 4 | 2–3 | 3½ | 4½ | 0 | 1 | 3 |
| | Powder | 4 at once | 4 | 4 | 2–3 | 4 | 5 | 3–3½ | 4 | 4½ | 0 | 2 | 3½ |
| Dolomite ..... | Lump | 1 then stops | 2 | 4 | 0 | 2 | 4 | 1¼–1 | 2 | 4 | 1 | 2 | 3 |
| | Powder | 2 | 3 | 4 | 0 | 3 | 4 | 1 | 2 | 4½ | 1 | 3 | 4 |
| Magnesite ..... | Lump | 2 | 3 | 5 | 2–1 | 2 | 4 | 2–1 | 2 | 4 | 2–1 | 3 | 4 |
| | Powder | 1 | 2 | 5 | 0 | 2 | 4 | 1 | 2 | 4½ | 1–2 | 3 | 5 |
| Cerussite ..... | Lump | 2–1–0 | 2 | 3 | 1 | 2 | 4 | 1–2 | 3 | 4½ | 1 | 2 | 3½ |
| | Powder | 1 | 1 | 2 | 3–0 | 3 | 4 | 2–2½ | 2½ | 4 | 1 | 3 | 3½ |
| Smithsonite.... | Lump | 0 | 2 | 3½ | 0 | 2 | 4–3½ | 0 | 2 | 4 | 0 | 2 | 4 |
| | Powder | 1 | 3 | 4½ | 0 | 2 | 4 | 0 | 2 | 4½ | 2 | 3 | 4½ |
| Witherite..... | Lump | 0 | 1 | 1 | 2 | 3 | 4 | 2½ | 3 | 4½ | 4–1 | 2 | 4 |
| | Powder | 1 | 1 | 1 | 3 | 4 | 5 | 3 | 4 | 5 | 4–1 | 2 | 4 |
| Strontianite ... | Lump | 3–1 | 1 | 3–1 | 1 | 3 | 4 | 2 | 3 | 4 | 1 | 3 | 4 |
| | Powder | 3 | 2 | 3 | 2 | 3½ | 4 | 3 | 4 | 5 | 3 | 4 | 4½ |
| Barytocalcite .. | Lump | 2½–2 | 3 | 3½ | 2 | 3 | 4 | 2½ | 4 | 5 | 3–1 | 2½ | 4 |
| | Powder | 3 | 3½ | 4 | 3 | 4 | 5 | 3 | 4½ | 5+ | 3–1 | 3 | 4 |
| Siderite ..... | Lump | 1 | 2 | 3–2 | 1 | 3 | 4–3½ | 2 | 2½ | 3½–3 | 0 | 2½ | 3½–3 |
| | Powder | 1 | 2½ | 3 | 1½ | 3 | 4 | 1 | 3 | 4 | 0 | 3 | 4½ |
| Malachite ..... | Lump | 3 | 4 | 4½ | 2 | 3 | 4 | 2½ | 3 | 4 | 2½ | 3 | 4 |
| | Powder | 3½ | 4½ | 5 | 3 | 4 | 5 | 3 | 4 | 5 | 3 | 4 | 4½ |
| Azurite ..... | Lump | 2½ | 3½ | 4½ | 0 | 2 | 3½ | 0 | 2 | 3½–3 | 1 | 2 | 3–2 |
| | Powder | 3½ | 4½ | 5 | 0 | 3 | 4 | 2 | 3 | 4 | 3–2 | 3 | 3 |
| Hydrozincite... | Lump | 3 | 4 | 5 | 3 | 3½ | 4½ | 2 | 2 | 3½–3 | 1½ | 2 | 3–2 |
| | Powder | 3½ | 4 | 5 | 3½ | 4½ | 5 | 3 | 3 | 4 | 1 | 2 | 2½ |
| Arazonite..... | Lump | 2½–2 | 2 | 3½–3 | 3 | 3½ | 4½–4 | 2 | 3½ | 4½ | 2–1–0 | 2 | 4–3 |
| | Powder | 3 | 3½ | 4 | 3 | 4½ | 5 | 3 | 4 | 5 | 3 | 3½ | 4½ |
| Phosgenite .... | Lump | 1 | 1 | 2 | 0 | 2 | 3 | 0 | 2 | 3–2 | 1 | 2 | 3–2 |
| | Powder | 2 | 2 | 2½ | 0 | 3 | 4–3 | 1 | 3 | 3½ | 2 | 2½ | 3–2 |
| Lansfordite .... | Lump | 3 | 4 | 5 | 3½ | 4 | 5 | 3½ | 4 | 5 | 3½ | 4 | 5 |
| | Powder | 4 | 4½ | 5 | 4 | 4½ | 5 | 4 | 4½ | 5 | 4 | 4½ | 5 |
| Rhodochrosite . | Lump | 1 | 2½ | 3–2 | 1 | 2½ | 3 | 0 | 2½ | 3½–2 | 1 | 2 | 3–2 |
| | Powder | 0 | 2 | 3½ | 0 | 2 | 3½–3 | 0 | 2½ | 3½–3 | 0 | 2 | 3½–3 |

5. Violently. 4. Strongly. 3. Freely, not strong. 2. Faintly, but plainly. 1. In traces. 0. No action.

*not strongly*, the rest being about half *strongly* and half *violently* affected. This reagent is satisfactory even in warm solution, and still better in hot solution.

Unlike citric acid, it causes dolomite to effervesce in traces even in the cold, while calcite is made to effervesce freely. The distinction is therefore not quite so sharp as with citric acid.

### CONCLUSION.

Tartaric acid is the best of the four reagents; citric acid is a close second. Both give satisfactory results in every case tested, using lump or powder in hot solution. Oxalic acid also gives effervescence in every case, in hot solution, and is indeed a practicable reagent, but not so strong as the preceding. Potassium acid sulphate is satisfactory except in the cases of witherite and phosgenite; the rest average low, but the effervescence is sufficient to be easily observed. Bearing these exceptions in mind, it can be used if the other reagents are not at hand.

Some sulphides also effervesce with each of the reagents, giving off hydrogen sulphide, as with hydrochloric acid, and the odor of the gas coming off should therefore be tested, to make sure that the material is not a sulphide.

LEHIGH UNIVERSITY,
January 18, 1900.

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## REGULATIONS FOR THE TESTING OF THERMOMETERS.[1]

[As Adopted by the Physikalisch-Technische Reichsanstalt, April 1, 1898.]

### I. PRELIMINARY REMARKS.

1. Glass thermometers filled with mercury, alcohol, toluene, or any other suitable liquid will be accepted for testing. They will be distinguished as:

*a*. Standard normal thermometers [*Haupt-Normalthermometer*];

*b*. Thermometers for scientific purposes (laboratory thermometers);

*c*. Thermometers for meteorological purposes and for estimating altitudes by boiling-point determinations;

*d*. Thermometers for technical purposes (factory thermometers);

[1] Translated for the use of the Committee on Standards and for the Journal of the Society by C. E. Linebarger.

*e*. Thermometers for medical purposes (clinical thermometers);

*f*. Thermometers for household or domestic use (window-, room-, bath-thermometers, etc.).

The *standard normal thermometers* will be tested only at the Physikalisch-Technische Reichsanstalt, the thermometers for household use only at the testing bureau in Ilmenau.

The Physikalisch-Technische Reichsanstalt is to decide as to the acceptance of thermometers other than the above, unless this is provided for in what follows, although questions as to acceptance may be addressed to the testing bureau at Ilmenau.

Such faults in the construction of all thermometers sent in to be tested, as may give rise to inaccuracies or irregularities in their temperature indications or render their reading too difficult are to be avoided.

**2.** The testing is done in two stages—the preliminary testing [*Vorprüfung*] and the main testing [*Hauptprüfung*]. The former takes into account all the regulations given in paragraphs 4 to 10, while the latter consists of a regular thermometric examination, beginning with observations, lasting for at least eight days, on the constancy of the indications of the thermometer (by means of determinations of the freezing-point and the like).

The type of the instrument determines whether the further tests shall involve:

*a*. A determination of the fundamental interval[1] by calibration and comparison with normal thermometers,

*b*. or only a comparison with normal thermometers in thermostats.

Whenever the divisions on the instrument permit, the amount of the depression of the freezing-point will always be determined and stated in the certificate.

In the testing of a maximum or minimum thermometer (for medical, meteorological, or other purposes), besides the comparison stated in *b*, experiments will be made to ascertain whether the instrument works properly. The errors in both series of tests for such thermometers should not differ when the divisions are

[1] [The fundamental interval is the scale interval between the normal boiling-point and the normal freezing-point, the latter being taken at the lowest position observed.]

$\frac{1}{10}°$ or $\frac{1}{5}°$ by more than 0.08° C.
$\frac{1}{1}°$ " $\frac{1}{2}°$ " " " 0.2° C.

The differences in the readings of maximum thermometers *at* a given temperature and *after* cooling, should not in the case of clinical thermometers amount to more than 0.15° C. In the case of maximum thermometers of other kinds the allowable differences are to be estimated from the length of the mercury column.

Tests will also be made to ascertain whether the device for recording the maximum temperature offers too great a resistance when the mercury is shaken down.

3. The fundamental temperature scale shall be that of the hydrogen thermometer as adopted for the international system of weights and measures according to a resolution of the *Bureau international des Poids et Mesures*, on October 15, 1887.

## II. GENERAL REGULATIONS.

4. The glass used in the construction of the thermometers should have the least possible thermal hysteresis [*thermische Nachwirkung*]. When glass is employed whose hysteresis is not sufficiently known or which is found to be too great, the thermometers must be allowed to stand from one to four months, the sender being notified of such action.

Thermometers which are to be tested at temperatures above 100° C., as well as all finer thermometers such as listed in paragraph 1, under *a*, *b*, and *c*, must be subjected to an artificial aging process before they are sent in. This consists in heating them for ten to thirty hours, according to the temperatures they are intended to indicate, to the highest temperature they register, and then cooling them slowly. Notice must therefore be given when the thermometers are sent in as to whether this heating has been done or not.

Thermometers reading to 550° C. should be made of Jena borosilicate glass $59^{III}$ or some similar difficultly fusible glass; those reading to 420° may also be made of Jena normal thermometer glass $16_{II}$ (with red-violet stripe) or of Greiner and Friedrichs' resistance glass (with blue stripe).

5. The capillary tube must be clean and of uniform bore. Thermometers of the types *a*, *b*, *c*, and *d*, in paragraph 1, are to have a pear-shaped bulb blown in their upper end. Bulbs blown

in the capillary tube itself must be there for a purpose and must not occasion a narrowing of the adjacent parts of the tube (unless, indeed, such constrictions are meant to serve a special object), which might cause a separation of the mercury during transportation or use. The upper end of the capillary must be in plain sight and not covered by the cap.

6. The mercury must be pure and dry and threads of it must not break off when it is retreating into the bulb. The mercury column should not separate at any place when the thermometer is inverted without jarring. Exceptions to this may be allowed in the case of thermometers with very long stems or large bores or with especially large bulbs.

Any other liquids used to fill the thermometers must be of such a nature that, when the column of liquid is retreating into the bulb, visible drops do not remain behind, and the coloring-matter that may be employed does not separate out.

The use of liquids with too low boiling-points is to be avoided as there is danger of their distilling over into the end of the capillary.

Thermometers designed to measure temperatures over 280° C. must be filled above the mercury with some dry gas (nitrogen, carbon dioxide, and the like) under proper pressure.

7. The scale-divisions must be durable and without any easily apparent errors. In the case of enclosed thermometers[1] [*Einschluss-thermometer*] the scale-divisions must be as close as possible to the capillary so as to insure definite and accurate readings at all positions.

The length of the shortest scale-division on a stem thermometer[2] [*Stab-thermometer*] should in general be at least $\frac{1}{6}$ of the circumference of the tube.

The nature of the division must be designated by the words *hunderttheilig* [" hundred-degreed "], Celsius, etc., and the divisions must be plainly numbered. Division marks must not be placed on widened parts of the capillary.

Division marks should not extend *unnecessarily far* above the temperature interval to be employed. Still a few divisions must

[1] Enclosed thermometers are such as have a small capillary tube lying against a scale and all enclosed in a larger tube.

[2] In stem thermometers the scale-divisions are cut or etched directly on the capillary tube.

always be marked above the highest and below the lowest of the parts of the scale to be tested.

Thermometers with Réaumur scales will not be tested. Exception to this rule will be made until the end of 1900 in the case of thermometers for technical use (*cf.* paragraph 1, *d*).

8. The scales of enclosed thermometers must be fastened securely and firmly, but must permit of free expansion without bending in one direction with reference to the enclosing tube. Thermometers with paper scales will be tested only up to 60° C.

The position of the scales with reference to the capillary or the enclosing tube is to be controlled by means of a mark which, when possible, will be placed on the *right-hand* side of the thermometer and is in no wise to interfere with the reading at that point.

The enclosing tube of enclosed thermometers should, unless exceptions be allowed according to the special regulations (paragraphs 11 to 16), be fused together at the upper end or be provided with a second mark in the vicinity of the end of the scale.

9. Only thermometers of the types *d* and *f* (technical and household thermometers) may have detachable scales. The tubes of such thermometers must be firmly fastened, must lie close to the scale, and must bear marks to control their position. The fastenings must be so arranged that they may be removed for testing and marking.

Thermometers with detachable scales will have both tube and scale marked (*cf.* paragraph 17).

10. Thermometers may bear the maker's number, trade-mark, etc., but nonsensical marks and such as are contrary to the results of the testing will not be permitted.

Maximum and minimum thermometers must be specially marked as such.

There must be on every thermometer sufficient room to place the official mark or stencil (*cf.* paragraph 17), and any other needed marks (*cf.* paragraph 18).

### III. SPECIAL REGULATIONS.

In what follows are given the requirements for testing and the allowable limits of error for the different types of thermometers listed in paragraph 1.

11. *Standard normal thermometers* must be mercury-in-glass thermometers, bearing the points 0 and 100 on their scale and must permit of direct calibration. They will be tested exclusively by the Physikalisch-Technische Reichsanstalt.

The divisions of these thermometers must be uniform and made without regard to the errors of calibration. The errors of division should not exceed $\frac{1}{20}$, and the width of a mark $\frac{1}{10}$, of the smallest interval.

The capillary tube must have a pear-shaped widening at its upper end and must be free from air. The examination of these thermometers will be made between the temperature-limits,—30° to + 100° C. and for every 10° at least.

The limits of error are:

1. For the fundamental interval, 0.10° C.;

2. For the error of calibration as the difference of the greatest deviations, 0.25° C.;

3. The depression of the freezing-point after a half-hour's heating to 100° C. and subsequent imbedding of the thermometer in ice for five minutes should not amount to more than 0.10° C.

The certificate will give in 0.001° the corrections for calibration, fundamental interval, freezing-point, and reduction to the gas-thermometer and also the aggregate error rounded off to 0.01.°

12. *Laboratory thermometers* are such as are employed in scientific and technical investigations in the laboratory for the measurement of temperatures from —80° to + 550° C.[1]

The limits of error are:

| For the temperature interval | When the scale is divided into integral degrees or multiples thereof. | fractions of a degree. |
|---|---|---|
| from — 80° to — 30° | 2° C. | 1.° C. |
| " — 30° " 0° | 1 | 0.5 |
| " 0° " 100° | 0.5 | 0.25 |
| " 100° " 200° | 1 | 0.5 |
| " 200° " 300° | 2 | 1 |
| " 300° " 400° | 3 | 2 |
| " 400° " 550° | 5 | 4 |

[1] Until further notice the scale of the air thermometer shall be standard for temperatures over 100° C., as the international agreement (*cf.* paragraph 3) has reference only to the interval between 0° and 100°, the comparison with the hydrogen thermometer having not yet been finished.

Tests are made when the divisions are in

$\frac{1}{10}$° C. for at least every 10°,

$\frac{1}{5}$° C. for at least every 15°,

$\frac{1}{2}$ or $\frac{1}{1}$° C. for at least every 20°, when the length of 10° is more than 40 mm.

$\frac{1}{2}$ or $\frac{1}{1}$° C. for at least every 25°, when the length of 10° is more than 20 mm. and less than 40 mm.

$\frac{1}{2}$ or $\frac{1}{1}$° C. for at least every 50°, when the length of 10° is more than 8 mm. and less than 20 mm.

$\frac{1}{2}$ or $\frac{1}{1}$° C. for at least every 100°, when the length of 10° is less than 8 mm.

13. (1) By *meteorological thermometers* are meant those used in finding the temperature of the air, of natural waters, of the earth's crust, of the sun's radiation, of the dew-point, etc. The scale may embrace any interval between —70° and + 100° C.

Tests are made

| When the divisions are in | | Limits of error. |
|---|---|---|
| $\frac{1}{5}$ or $\frac{1}{10}$° C. | For every 10°, at least. | Same as given in |
| $\frac{1}{2}$ " $\frac{1}{1}$° " | " " 20°, " " | paragraph 12. |

(2) Thermometers for the measurement of altitudes by boiling-point determinations may be divided either in centigrade degrees or in millimeters of tension of water-vapor under various pressures and may embrace the interval + 70 to 102° C.; they may also have an auxiliary scale near the zero-point. To prevent as much as possible any changes in these thermometers when used for some time on scientific expeditions, they should be subjected to an artificial aging process (*cf.* paragraph 4) before they are sent in.

Tests will be made for every 4°, at least, or in case a millimeter scale is used, for every 50 mm. The errors should not exceed 0.1° C. or 3 mm. respectively. If an auxiliary scale be attached at 0°, the depression of the freezing-point will be determined after the thermometer has been heated for half an hour to 100°; it should not amount to more than 0.1° C. If, however, an auxiliary scale is not attached, the depression of one of the lowest points of the scale will be determined.

14. The testing of *thermometers for technical purposes*, because of the multiplicity of their forms and the unusually large

dimensions of some of them, can be undertaken only as the facilities at hand permit.

The limits of error for these thermometers may be double those given in paragraph 12.

Thermometers made of glass free from thermal hysteresis up to 100° C. whose errors are all less than 0.05° C. are termed free from error. The number of points on the scale that will be tested is fixed according to the regulations given in the same paragraph, unless the thermometers be uncommonly long.

In the case of long technical thermometers the capillary connecting the bulb and scale must be so fine that the indications of the thermometer will not be appreciably affected by the temperature of the neck, due regard being given to the degree of accuracy required of such thermometers. If tests are to be made at higher temperatures on factory thermometers having long necks whose volume cannot otherwise be reliably ascertained, they must be sent in before they are filled under pressure so that the volume of the connecting capillary can be determined.

15. *Has to do with the limits of error, etc., of clinical thermometers.*

16. *Treats of limits of error, etc., of household thermometers.*

## IV. CERTIFICATES, CHARGES AND TIME REQUIRED FOR TESTING.

17. Thermometers with which certificates are given will be marked to show that they have been tested by the Physikalisch-Technische Reichsanstalt with the Imperial Eagle (*Reichsadler*) and P T R, and to show that the testing has been done at Ilmenau, with the Imperial Eagle and G S.

They are also marked with a number, with which *all* thermometers with the exception of such clinical thermometers as have been found unsuitable for testing are provided.

In addition, the year is given for all thermometers listed in paragraph 1, under *a*, *b*, *c*, and *d*.

Besides the thermometric errors, the certificate contains indications, when necessary, as to the kind and application of the thermometer in question.

The rounding-off of the thermometric errors found by the tests depends upon the nature of the scale and the results of the

testing, except where a special procedure is prescribed for the individual classes of thermometers in the foregoing regulations.

As a rule the errors observed are given for the thermometers in a vertical position and with the *whole* of the liquid column immersed in the bath.

If the use of the thermometer requires the liquid column to emerge from the bath whose temperature is to be measured, information must be given when the thermometer is sent in, as to how deep the thermometer must dip into the bath and what the temperature of the emergent column may be assumed to be.

18. *Charges for testing.*

19. Thermometers will be tested in the order of their receipt as shown by the post-mark; the preliminary tests will be made at once upon the receipt of the thermometer. The tests will be finished in from three to four weeks according to their nature and the amount of work on hand.

APPENDIX.

20. *Recommendations as to the packing and sending of thermometers.*

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 19.]

## A NEW SYNTHESIS IN THE QUINAZOLINE GROUP.[1]

(PRELIMINARY ANNOUNCEMENT.)

BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF.

Received February 15, 1900.

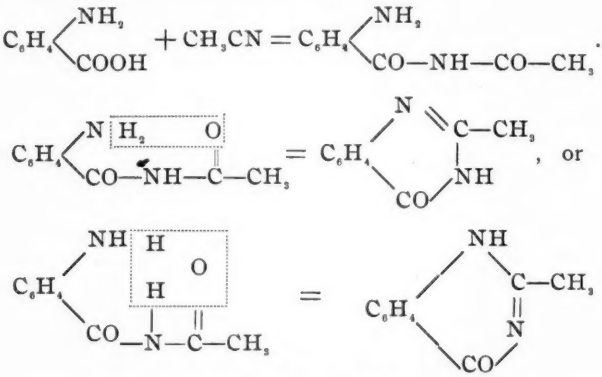
IN the course of some researches carried on in this laboratory by J. A. Mathews on "The Action of Nitriles upon Aromatic Acids,"[2] it was discovered that when anthranilic acid and acetonitrile were heated together in a sealed tube for five hours at 220°–230° C., instead of obtaining orthoamidobenzonitrile as expected, there resulted a crystalline product melting at 232°. This body was boiled with strong hydrochloric acid, and the solution on cooling deposited long needles which sublimed at about 280° without melting. Not enough of the substance, however, was secured for an analysis, and hence its nature could not be determined.

[1] Read before the New York Section, February 9, 1900.

[2] This Journal, 20, 654.

The writers have continued this investigation, and, by varying the conditions slightly, have readily obtained very fair yields of this substance and identified it as the 2-methyl-4-ketodihydroquinazoline first described by Weddige[1] and later obtained by Bischler and Burkart,[2] Bischler and Lang,[3] and Niementowski[4] The needles obtained by Mathews by the action of hydrochloric acid were, of course, only the HCl salt.

The reaction by which the quinazoline compound is produced from anthranilic acid and acetonitrile is easily explained when it is remembered that, under conditions of heat and pressure, a nitrile tends to combine with an organic acid to form a secondary amide, as shown first by Gautier,[5] and later, in this laboratory, confirmed by the work of Colby and Dodge.[6] The reaction, therefore, probably takes the following course :



As early as 1860, Griess and Leibius[7] studied the action of cyanogen gas upon the amidobenzoic acids, and in 1869, Griess[8] obtained condensation products by passing cyanogen gas into aqueous and alcoholic solutions of anthranilic acid. The condensation products, however, were due entirely to a preliminary

1 *J. prakt. Chem.* (2), **31**, 124.
2 *Ber. d. chem. Ges.*, **26**, 1350.
3 *Ibid.*, **28**, 282.
4 *J. prakt. Chem.* (2), **51**, 564; and *Ber. d. chem. Ges.*, **29**, 1360.
5 *Zischr. Chem.* (1869), 127.
6 *Am. Chem. J.*, **13**, 1.
7 *Ann. Chem.* (Liebig), **113**, 332.
8 *Ber. d. chem. Ges.*, **2**, 415.

amidine union between the cyanogen and amido groups, which in our synthesis is very improbable, both on account of the less acid character of the nitriles employed and also because Bernthsen has shown[1] that benzonitrile and aniline have no appreciable action upon each other even at 360° C. The products obtained would also be far different from those which we have separated.

The reaction of Niementowski,[2] by which he obtains quinazoline derivatives through the interaction of an amide upon anthranilic acid, appears to be a simultaneous condensation between the amido and carbonyl groups of the amide and the carboxyl and amido groups of the anthranilic acid, and is, possibly, in its internal mechanism, somewhat related to the nitrile synthesis under discussion. Niementowski found, however, that while the yield with formamide and acetamide was excellent, as the molecular weight of the amide increased it became less and less satisfactory, the higher temperature required producing more and more decomposition, and consequently more by-products, while with benzamide the condensation failed entirely and no quinazoline body could be obtained.

With our synthesis, on the other hand, using nitriles instead of amides, the reaction proceeds just as smoothly with aromatic nitriles as with aliphatic; the contents of the tubes are invariably crystalline and free from by-products (except a small amount of carbonaceous material), and by treating with boneblack and crystallizing twice from alcohol, the quinazoline body is obtained pure. We have thus prepared with the greatest ease the following derivatives of the 4-ketodihydroquinazoline, together with many of their salts:

*2-Methyl.*—Identical with that described by Weddige.[3]

*2-Ethyl.*—Already described by Bischler and Lang,[4] and by Niementowski.[5]

*2-Phenyl.*—Isomeric with, but not the same as the phenyl derivative of Körner,[6] the isomerism probably being due to a different position of the double bond in the miazine nucleus (at (1), instead of (2) ?).

1 *Ann. Chem.* (Liebig), **184**, 349, foot-note.
2 *J. prakt. Chem.* (2), **51**, 564.
3 *Ibid.* (2), **31**, 124.
4 *Ber. d. chem. Ges.*, **28**, 284.
5 *J. prakt. Chem.* (2), **51**, 568.
6 *Ibid.* (2), **36**, 155.

*2-Benzyl.*—New.

*2-Paratolyl.*—New.

The description of these bodies and their derivatives, together with many others upon which we are now at work, will be presented later. So much work has been and is being done upon quinazolines that we have deemed it wise, before entering upon the very extensive field which this new synthesis opens up, to present this preliminary notice, that we may be left free to continue our work without fear of molestation.

We should like, therefore, to reserve for the Organic Laboratory of Columbia University, the study of the action of cyanogen compounds upon organic acids, as we shall endeavor to extend this research to bodies of the aliphatic series (in the hope of obtaining oxypyrimidine compounds), as well as to other classes of compounds. We are also investigating the action of nitriles upon other ortho-substituted acids, etc., and upon closely related bodies.

When one considers the ease with which the nitriles can be obtained, especially in the aromatic series, and the fact that all the nitriles used so far, both aliphatic and aromatic, react with the same facility, it does not seem too much to say that this new process appears likely to prove the most widely applicable and most important synthesis for quinazoline compounds yet discovered.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, February 1, 1900.

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## A COMPARISON OF SOME FORMALDEHYDE TESTS.[1]

BY B. M. PILHASHY.

Received February 5, 1900.

HAVING had occasion to make some qualitative tests to show the presence of formaldehyde, I reviewed the recent chemistry for the detection of formaldehyde. In some instances the reaction given for formaldehyde proved to be true for other aldehydes also and apparently for distilled water. In some cases the delicacy of the reaction given for a particular reagent was not true for the stated dilution, while in others the reaction was clear and not to be doubted. The following summary of

[1] Read before the Cincinnati Section, November 15, 1899.

various reactions for the more common aldehydes may prove useful to others, who may have occasion to work in the same line.

(*a*) *Schiff's Reagent.*—Most aldehydes in dilute solutions give a violet coloration with this reagent. (Fuchsin decolorized by sulphurous acid.) This can also be obtained by mere exposure of the reagent to the air or by warming the suspected liquid with the reagent even in the absence of an aldehyde.[1]

(*b*) *Phenol and Sulphuric Acid.*—Most aldehydes give with very dilute phenol and sulphuric acid added to form a layer beneath, a scarlet ring changing to dark red on heating.[2]

(*c*) *Diazobenzenesulphonic Acid.*—Most aldehydes with this reagent in the presence of free alkali and sodium amalgam give an intense violet color at once or within twenty minutes. The colors are destroyed by exposure of by acid.[3]

(*d*) *Nessler's Solution.*—Acetaldehyde as well as formaldehyde gives a precipitate with Nessler's solution. They also give a precipitate with anilin.[4]

(*e*) *Dimethylanilin and Sulphuric Acid.*—Trillat gives the following reaction for formaldehyde alone. To a dilute solution a few drops of sulphuric acid and also of dimethylanilin are added. The mixture is heated for half an hour on a water-bath, made alkaline and further heated to drive off the excess of dimethylanilin which can be detected by its odor. The liquid is then filtered and the paper moistened with acetic acid. If formaldehyde is present, a blue coloration results when lead dioxide is then sprinkled on the paper.[5]

The following experiments tend to show that this reaction is due to dimethylanilin present.

*Experiment 1.*—If a piece of filter-paper be moistened with a very dilute solution of dimethylanilin in water it will give the blue color reaction with lead dioxide and acetic acid.

*Experiment 2.*—Twenty cc. distilled water, 2 drops of sulphuric acid, and 1 drop of dimethylanilin were mixed, forming

1 Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 217.
2 *Ibid.*
3 *Ibid.*
4 *Ibid.*
5 *Ibid.*, p. 220.

a very dilute acid solution. This was heated one-half hour, during which time 100 cc. distilled water were added at intervals to replace that evaporated. After heating a while a strip of filter-paper dipped into this solution gave a yellow color with lead dioxide and acetic acid. Another strip dipped into the solution and made alkaline with ammonium hydroxide or sodium carbonate solution gave a slight blue after ten minutes. At the end of the heating these reactions could not be again obtained pointing to a probable volatilization of the salt formed.

*Experiment 3.*—Instead of the distilled water in Experiment 2, 20 cc. formaldehyde solution (1 : 1000) were used. After heating for one-half hour a strip of filter-paper moistened with the solution gave the yellow color observed in Experiment 2, with the lead peroxide and acetic acid and the blue color with the same reagents after making alkaline. The outside of the dish was coated with a yellow salt which was washed into a dish, made alkaline and filtered. The filter-paper gave the beforementioned blue reaction.

*Experiment 4.*—A few drops of dimethylanilin were dissolved in water with the aid of a few drops of sulphuric acid. A strip of paper moistened with it gave the yellow reaction with lead peroxide and acetic acid. The solution was neutralized and filtered. The filter-paper as well as a strip moistened with the solution gave the blue coloration as above.

*Experiment 5.*—Twenty cc. formaldehyde solution (1 : 1000), 2 drops of sulphuric acid, and 1 drop of dimethylanilin were heated for one-half hour, made alkaline with sodium hydroxide solution and then heated for one hour longer to drive off any free dimethylanilin in excess. There was no odor to the solution which was filtered. The filter-paper gave no blue coloration with lead peroxide and acetic acid.

## SUMMARY.

From the foregoing experiments it seems that Trillat's test does not show the presence of formaldehyde, but of dimethylanilin or its salts when not completely volatilized.

(*f*) *Lebbin's Test.*[1]—This is said to be delicate enough to detect 1 part formaldehyde in 10,000,000 of water. In my experience 1 in 200,000 seems to be the limit.

(*g*) *Morphin hydrochloride*[2] with sulphuric acid is not to be considered sensitive enough for formaldehyde in a more than 1 : 1000 solution, a purple ring being obtained.

(*h*) *Phenylhydrazin hydrochloride*[3] seems to be the best reagent for formaldehyde. The solution of 1 gram of phenylhydrazin hydrochloride with 1.5 grams sodium acetate in 10 cc. water is used. To 1 cc. of the liquid 2 drops of the reagent and 2 drops of sulphuric acid are added producing a green coloration. In as dilute a solution as 1 : 10,000 or 1 : 100,000, 3 cc. of the liquid with 4 drops of the reagent and 4 drops of sulphuric acid heated for half a minute bring out the color. For 1 : 250,000, 3 cc. of the liquid with 5 drops of the reagent and 5 drops of sulphuric acid heated for about a minute, give a very light tinge of green after three minutes, a decided tint after ten minutes.

(*i*) Rimini[4] uses *phenylhydrazin hydrochloride with sodium nitroprusside and concentrated sodium hydroxide*, a blue coloration resulting. One part in 1,000 and 1 in 10,000 give an intense blue when 1 cc. of the solution is mixed with 2 drops each of phenylhydrazin hydrochloride solution and of sodium nitroprusside solution, 1 cc. of caustic soda solution being then added. One in 100,000 gives a deep blue, and one in 1,000,000 gives a light blue. These blues change quickly to green, yellow, light brown, and red. A peculiarity is the rise of the red color to the top leaving a yellow layer below. Both layers are clear solutions. If the same amount of reagent as given above be added to dilutions greater than 1 in 1,000,000, about the same shade of blue is obtained for them,—hence the limit seems to be 1 in 1,000,000.

[1] Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 220.
[2] *J. Soc. Chem. Ind.*, Abst., p. 955 (1898).
[3] *Ibid.*, p. 954.
[4] *Ibid.*, p. 697.

[Contributions from the Havemeyer Laboratories of Columbia University, No. 20.]

# SOME NEW TELLURIUM COMPOUNDS.

By Victor Lenher.

Received January 27, 1900.

IN many points tellurium resembles selenium in its derivatives, the oxides are not unlike in their behavior, and the tellurites and tellurates are very similar to the corresponding selenites and selenates.

Tellurium, owing to its high atomic weight, shows greater stability in its higher halogen derivatives than the preceding members of the group to which it belongs. Two series of halides are known, corresponding to $TeX_2$ and $TeX_4$. The tetrahalides are those most commonly met with and seem to be the type which tellurium tends to follow with the halogens. With selenium, on the contrary, we find the lower halides are the more stable. Heat transforms the tetra- into the monohalides with corresponding loss of halogen.

As in the case of the other natural groups of elements, the basic property is found to increase with the rise in atomic weight, so here also we find the same tendency in the higher members to be more basic than the lower ones. Sulphur is a decidedly acid element; in selenium this property is decidedly weaker, while with tellurium we actually find such salts as the tartrate, basic sulphate, and basic nitrate, which are not known in the case of a true non-metal. In appearance, tellurium resembles a metal, while sulphur and selenium, in the elementary condition, certainly do not appear metallic.

As a result of this increase in basic properties, we should expect to find that tellurium forms better defined double halides than selenium. This is actually the case. Only the double bromides of selenium are known. Attempts to prepare double chlorides thus far have proved unsuccessful, and likewise the formation of double bromides of selenium is restricted within certain limits.

It has been shown by the author[1] that selenium tetrabromide can unite with the hydrobromides of the organic amines to form

[1] This Journal, 20, 572.

well-defined double salts in which the amine plays the rôle of ammonia in the compound $(NH_4)_2SeBr_6$. Norris[1] has also prepared a number of the double halides of selenium.

When tellurium replaces selenium in the double halides, we obtain more clearly defined compounds than is the case with the latter. In fact, while selenium tetrabromide unites with only the hydrobromides of the fatty amines and with the hydrobromides of pyridine and piperidine, no compound could be prepared with any of the true aromatic amines or with quinoline; neither has it been possible to prepare an aromatic or aliphatic amine salt in which selenium tetrachloride replaces the tetrabromide.

Both tellurium tetrabromide and tetrachloride form a series of beautiful salts with the aliphatic amines, and both of the halides also unite with the aromatic amines to form well-defined derivatives. In the series of salts which has been prepared, it is somewhat striking to notice that all the bromides are red while the chlorides are invariably yellow. Wheeler[2] has shown that the double chlorides of tellurium with potassium, rubidium, and cesium are yellow while the corresponding bromides are red.

To prepare the salts it is only necessary to add a solution of tellurium dioxide in hydrochloric or hydrobromic acid to the amine salt dissolved in the corresponding acid; a precipitate of the double salt generally forms immediately, and this precipitate, when recrystallized from dilute acid, gives crystals of the salt in a purified condition.

All the double salts are decomposed by pure water with the formation of hydrated $TeO_2$, but are soluble in dilute acids and in alcohol.

*Method of Analysis.*—Great difficulty was at first experienced in making an analysis of these compounds, owing to the complications which invariably ensued. The method which was finally adopted consisted in dissolving a weighed quantity of the salt in a dilute solution of tartaric acid, adding to this a measured excess of standard silver nitrate and a few drops of ferric alum. The solution was then treated with a standard solution of ammonium thiocyanate. The object of the tartaric acid was

[1] *Am. Chem. J.*, 20, 490.
[2] *Ztschr. anorg. Chem.*, 3, 428.

to hold in solution the tellurium dioxide, which otherwise would be precipitated by the water, and to prevent the formation of a precipitate of silver tellurite which would interfere with the titration. When a sufficient quantity of tartaric acid is present to hold tellurium dioxide in solution and prevent its action on the silver, the method proves very accurate. The silver nitrate solution was made up of such strength that 1 cc. = 0.007969 gram bromine or 0.003533 gram chlorine.

*Methylamine Bromotellurate*, $(CH_3NH_3)_2TeBr_6$.—To a solution of methylamine in hydrobromic acid, a hydrobromic acid solution of $TeO_2$ was added, when a red precipitate immediately formed. This was collected on a filter and the salt purified by recrystallization from dilute hydrobromic acid.

0.3023 gram salt required 27.1 cc. silver nitrate solution.

| | Calculated for $(CH_3NH_3)_2TeBr_6$. | Found. |
|---|---|---|
| Br | 71.50 | 71.44 |

The crystals are of a red color and are regular octahedrons, having a high index of refraction.

*Methylamine Chlorotellurate*, $(CH_3NH_3)_2TeCl_6$.—This substance was prepared in a manner similar to the preceding; that is, a hydrochloric acid solution of tellurium dioxide was added to a solution of the amine in hydrochloric acid and the product recrystallized from dilute hydrochloric acid.

0.3029 gram salt required 44.9 cc. silver nitrate solution.

| | Calculated for $(CH_3NH_3)_2TeCl_6$. | Found. |
|---|---|---|
| Cl | 52.67 | 52.37 |

The crystals appear as yellow hexagonal plates, with a micaceous cleavage. The index of refraction is low, and in polarized light a low order of colors is shown.

*Ethylamine Bromotellurate*, $(C_2H_5NH_3)_2TeBr_6$.—Exactly the same procedure was adopted in the preparation of this salt as with the methylamine derivative.

0.3056 gram salt required 26.3 cc. silver nitrate solution.

| | Calculated for $(C_2H_5NH_3)_2TeBr_6$. | Found. |
|---|---|---|
| Br | 68.63 | 68.58 |

The crystals are red hexagonal plates which show a strong

basal cleavage. In polarized light the colors are of a low order, and the refractive index is fairly high.

*Ethylamine Chlorotellurate*, $(C_2H_5NH_3)_2TeCl_6$.—This salt forms yellow hexagonal plates showing a strong cleavage, and in polarized light showing a low order of colors.

0.3034 gram salt required 42.1 cc. silver nitrate solution.

| | Calculated for $(C_2H_5NH_3)_2TeCl_6$. | Found. |
|---|---|---|
| Cl | 49.24 | 49.02 |

*Trimethylamine Bromotellurate*, $[(CH_3)_3NH]_2TeCl_6$.—This salt is the most strongly crystalline of all the compounds prepared. It forms red orthorhombic crystals which have a fairly high index of refraction. The crystals show a low order of colors in polarized light, but in convergent light a biaxial figure is readily seen.

0.3029 gram salt required 24.9 cc. silver nitrate solution.

| | Calculated for $[(CH_3)_3NH]_2TeBr_6$. | Found. |
|---|---|---|
| Br | 65.98 | 65.51 |

*Aniline Bromotellurate*, $(C_6H_5NH_3)_2TeBr_6$.—The action of the bromide of tellurium on aniline hydrobromide is quite unlike that of selenium tetrabromide. In the case of selenium, no compound seems to be formed, the aniline actually reducing the bromide of selenium even in acid solution.

When a solution of tellurium dioxide in hydrobromic acid is added to aniline hydrobromide, a red precipitate forms, which can be purified by recrystallization from dilute hydrobromic acid. The salt then appears as red monoclinic tablets which act strongly on polarized light.

0.3053 gram salt required 23.3 cc. silver nitrate solution.

| | Calculated for $(C_6H_5NH_3)_2TeBr_6$. | Found. |
|---|---|---|
| Br | 60.34 | 60.82 |

*Aniline Chlorotellurate*, $(C_6H_5NH_3)_2TeCl_6$.—While selenium tetrabromide does not enter into combination with aniline hydrobromide, tellurium tetrabromide as has been seen, readily forms a double salt. The formation of double chlorides with selenium remains yet to be shown, while here we have the first example of the union of tellurium tetrachloride with the salt of an aro-

matic amine. This salt, which was prepared in a manner similar to the preceding is, like all of the chlorides, yellow in color. The crystals of the salt were too small to determine their form, but they are active to polarized light. The salt is very light and feathery.

0.3017 gram salt required 34.2 cc. silver nitrate solution.

| | Calculated for $(C_6H_5NH_2)_2TeCl_6$. | Found. |
|---|---|---|
| Cl | 40.25 | 40.04 |

*Pyridine Bromotellurate*, $(C_5H_5NH)_2TeBr_6$.—This compound forms fine red crystals, not large enough to determine the crystallographic system of the salt, but it was found to be active to polarized light.

0.3041 gram salt required 24.1 cc. silver nitrate solution.

| | Calculated for $(C_5H_5NH)_2TeBr_6$. | Found. |
|---|---|---|
| Br | 62.55 | 63.15 |

*Pyridine Chlorotellurate*, $(C_5H_5NH)_2TeCl_6$.—This salt forms yellow isometric crystals having a low index of refraction. The crystals were very small.

0.3012 gram salt required 36.2 cc. silver nitrate solution.

| | Calculated for. $(C_5H_5NH)_2TeCl_6$. | Found. |
|---|---|---|
| Cl | 42.54 | 42.46 |

*Quinoline Bromotellurate*, $(C_9H_7NH)_2TeBr_6$.—Very small red crystals of the salt were obtained, which were found to act on polarized light.

0.3026 gram salt required 21.00 cc. silver nitrate solution.

| | Calculated for $(C_9H_7NH)_2TeBr_6$. | Found. |
|---|---|---|
| Br | 55.32 | 55.30 |

*Quinoline Chlorotellurate*, $(C_9H_7NH)_2TeCl_6$.—The crystals of this salt were also very small and were active to polarized light.

0.3051 gram salt required 30.6 cc. silver nitrate solution.

| | Calculated for $(C_9H_7NH)_2TeCl_6$. | Found. |
|---|---|---|
| Cl | 35.44 | 35.43 |

It thus appears that both the tetrachloride and tetrabromide of tellurium readily form double salts with the salts of both the fatty and the aromatic amines. The salts crystallize well,

and their color seems to be dependent on the halogen content, the bromides being invariably red, and the chlorides yellow.

A solution of tellurium dioxide in halogen acids gives a precipitate with nearly all of the alkaloids, probably forming salts similar to those above described. The alkaloid derivatives are now being studied in this laboratory.

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## THE ACTION OF α-ACYLATED PHENYLHYDRAZINES ON THE CHLORINE DERIVATIVES OF QUINONES.

(PRELIMINARY REPORT.)

BY WILLIAM MCPHERSON AND ROBERT FISCHER.

Received January 29, 1900.

THE investigations of Zincke[1] on the interaction of phenylhydrazine and the quinones led to the general result that α-naphthoquinone, β-naphthoquinone, and phenanthraquinone condense in a normal manner with phenylhydrazine, but that under similar conditions, all of the quinones of the benzene series give hydroquinones, the reaction being attended with gas evolution. Many subsequent efforts have been made to effect a normal condensation between benzoquinone and phenylhydrazine, since this reaction would help to solve the problem of the constitution of the oxyazo-bodies. Although this has not as yet been accomplished, it has been shown by one of us[2] that the unsymmetrical acylated phenylhydrazines, *e. g.*, $C_6H_5N.C_7H_5O.NH_2$, condense with benzoquinone in a normal manner forming a hydrazone derivative in accordance with the following equation :

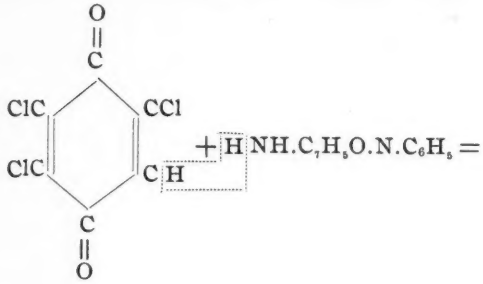
$$C_6H_4\begin{matrix}O\\O\end{matrix} + H_2N.C_7H_5O.N.C_6H_5 = C_6H_4\begin{matrix}O\\N—C_7H_5O.N.C_6H_5\end{matrix}.$$

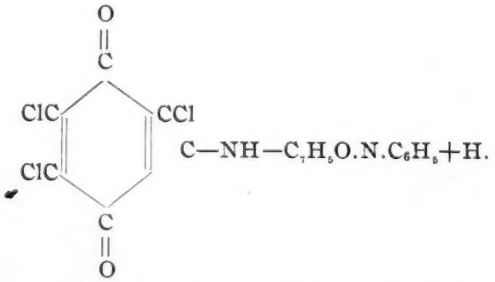
This reaction has recently been extended to the chlorine derivatives of quinone. It has been found, however, that while the α-acylphenylhydrazines react with these readily, the compounds formed are not hydrazones but *hydrazino* derivatives, possessing a structure similar to the so-called anilidoquinones, formed by the interaction of quinones and aniline under certain conditions. With trichlorbenzoquinone the following reaction

[1] *Ber. d. chem. Ges.*, 16, 1563.

[2] *Ibid.*, 28, 2414; *Am. Chem. J.*, 22, 364.

takes place, the two hydrogen atoms being removed by the oxidizing action of a second molecule of the quinone.




This reaction is analogous to the interaction of trichlorquinone and aniline, investigated by Niemeyer,[1] the point of attack being the hydrogen of the quinone in preference to the chlorine.

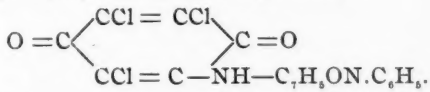
Tetrachlorquinone gives with $\alpha$-benzoyl phenylhydrazine the same product as trichlorquinone, hydrochloric acid being evolved.

It is quite probable that under different conditions, hydrazone derivatives of the chlorquinones may be obtained. This subject is now under investigation in this laboratory. The interaction of the quinones and the unsymmetrical naphthylhydrazine derivatives is also being studied with the hope of isolating both the true oxyazo-bodies and their isomeric quinonehydrazones and thus definitely deciding the constitution of the so-called free oxyazo-bodies.

[1] *Ann. Chem.* (Liebig), **228**, 322.

## EXPERIMENTAL PART.

*Action of α-Benzoyl Phenylhydrazine on Trichlorbenzoquinone.*—α-Benzoyl phenylhydrazino trichlorquinone,



The hydrazine was prepared according to Widman's excellent method,[1] for the preparation of unsymmetrical hydrazines. Some slight changes in the process were found advantageous. In the case of α-benzoyl-β-acetylphenylhydrazine the following method easily gives the pure solid product, in place of the difficultly solidifying oil which Widman first obtained. To 10 grams of pure β-acetylphenylhydrazine were added 70 grams of benzene and 9.4 grams of benzoyl chloride. The flask was connected with a return condenser and its contents heated to boiling. The hydrazine slowly dissolved with evolution of hydrochloric acid. After heating for a few minutes the α-benzoyl-β-acetylphenylhydrazine began to separate on the sides of the flask owing to the slight solubility of the body in benzene. After heating for one hour, the reaction was complete. On cooling, the product was removed by filtration, and was obtained pure (m. p. 152°–153°) by a single crystallization from alcohol diluted with an equal volume of water. The yield is nearly quantitative. From this the difficultly soluble sulphate $(C_6H_5.NC_7H_5O.NH_2)_2H_2SO_4$ was prepared by saponification as directed by Widman. In the first experiments the free base was obtained from this sulphate and then converted into the soluble hydrochloride. In the later experiments, however, it was found advantageous to use the original sulphate, dissolving it in water to which was added just enough alcohol to effect solution.

Four grams of trichlorquinone and 7 grams of α-benzoylphenylhydrazine sulphate in a finely divided condition were placed in a flask and 300 cc. of water, 140 cc. of alcohol, and a few drops of sulphuric acid added. The flask was connected with a return condenser and the contents boiled for five minutes. The red powder which separated was then filtered from the hot liquid and dried on a clay plate (yield 5 to 6 grams). The body was

[1] Monograph "Ueber asymmetrische Secundäre Phenylhydrazine," published by the "Gesellschaft der Wissenschaften" at Upsula 1893; also *Ber. d. chem. Ges.*, 26, 945.

easily purified by crystallizing from benzene, or from benzene-ligroin. Melting-point 158.5°.

1. 0.1641 gram substance gave 0.1668 gram silver chloride.

2. 0.2115 gram substance gave 0.2127 gram silver chloride.

1. 0.2397 gram substance gave 0.4714 gram carbon dioxide and 0.0620 gram water.

2. 0.2484 gram substance gave 0.4891 gram carbon dioxide and 0.0619 gram water.

| | Calculated for $C_{19}H_{11}N_3O_3Cl_3$. | Found. 1. | 2. |
|---|---|---|---|
| C | 54.09 | 53.63 | 53.69 |
| H | 2.63 | 2.87 | 2.76 |
| Cl | 25.23 | 25.13 | 24.86 |

α-Benzoyl phenylhydrazino trichlorquinone is a bright red crystalline body, readily soluble in hot benzene and alcohol, from each of which it crystallizes in long rectangular prisms or in star-shaped groups of small prisms. It is sparingly soluble in ligroin, and practically insoluble in glacial acetic acid and dilute caustic soda solution. Its action with phenylhydrazine is similar to that of quinone, decomposition occurring with evolution of gas. By dissolving in concentrated sulphuric acid as well as by the action of alcoholic potash, the benzoyl group is split off, but some further reaction takes place forming a dark brown crystalline body. This is soluble in caustic soda and melts with decomposition at 198°. Its structure has not yet been determined.

OHIO STATE UNIVERSITY, January, 1900.

## NOTE ON A METHOD OF STANDARDIZING WEIGHTS.

BY THEODORE WILLIAM RICHARDS.

Received February 26, 1900.

ALTHOUGH nowadays it is possible to procure, for a comparatively small sum, sets of weights which are reasonably exact, it is recognized that for gravimetric work demanding any considerable degree of accuracy, corrections on account of occasional errors in the weights must be applied. It is obvious, moreover, that if the relative values of the weights in an inexpensive box are known, this set may serve a purpose which would otherwise demand a much more expensive one. For ten years every student in quantitative analysis at Harvard has been required to standardize his weights; and since the method

adopted has some peculiarities, not described in the usual directions for this purpose,[1] it is explained below. This method does not pretend to be especially original; the reason for its publication is simply a desire to advance the cause of accuracy.

According to our method the weights to be standardized are weighed wholly on one side of the balance, the comparison being made by substitution. This procedure, of course, eliminates a possible inequality in the length of the arms of the balance, which must otherwise be computed. A more important advantage is the fact that it also obviates the mental confusion resulting from the continual interchanging of weights between the opposite pans. Thus is avoided one of the common sources of error in the beginner's work.

It is, of course, necessary that all of the fractional weights should, taken together, constitute a gram; and because the milligram weights are never used, it is convenient to add an extra centigram weight from another set to supplement the other small weights. The different weights of the same denomination should be marked in a recognizable way, and should always be arranged in the same order in the box. The comparison usually begins with centigrams and proceeds upwards. One of the centigram weights is placed upon the *left-hand* scale-pan, and is balanced by any suitable tare, care being taken that the rider is not too near either end of its path.[2] The zero point of the balance need not have been taken in the first place. The swings of the balance with its centigram load are now carefully noted and then another centigram weight is substituted for the first. Obviously, the amount by which the rider must be moved to attain the same position of equilibrium gives at once the difference between the two weights; and even the neophyte could hardly err as to its sign. Of course, instead of moving the rider, the difference may be calculated from the change in the swings; or both swings and rider may be used. The first weight is then replaced upon

[1] For the usual method adopted by Kohlrausch, see Ostwald's Handbook of Phys. Chem. Measurements (Walker), p. 41.

[2] A crude set of weights is, of course, the most convenient tare, and a 5 milligram weight may be kept on the left-hand pan so that the rider may assume a convenient position. The use of the *left-hand* scale-pan for the weights to be standardized renders a confusion of the sign of the correction less likely, because the rider is on the right. In this case, the *weights are the objects to be weighed*, and hence naturally take the left-hand position.

the left-hand pan, and if the swings correspond to the first observation it is reasonably certain that the balance has remained in a constant condition throughout the trial, and hence that the difference between the two weights has been accurately determined. In this way every weight is compared with every other weight of the same denomination, as well as with the combination of all the smaller weights. Thus are obtained a number of independent equations one less than the number of weights; and by assuming the value of any one of the weights the others may all be calculated.[1]

We have found it most convenient for the purposes of calculation to make the temporary assumption that the first centigram weight is correct. From it by the simplest possible process of addition and subtraction may be built up quickly the values of all the other weights. While the values thus computed are wholly consistent among themselves, they are usually far too different from the face values of the weights for convenient use. The reason of this is because the assumed standard is so small a quantity. It is necessary then to translate these consistent values into other terms by dividing every value by the value of one of the larger weights, to be taken as the new and permanent standard.[2]

This division (which would demand six or seven place logarithm tables for the larger weights) is conveniently replaced, however, by a simple method depending upon the properties of small numbers in presence of large ones.[3] It is quite sufficiently accurate to compare the value of each weight with the corresponding aliquot part of the value of the weight to be taken as a final standard. The difference between the actual value and the ideal value will give at once the correction to be applied to the weight.

[1] Of course, many extra equations, which are not independent of the others, are obtained by the literal fulfilment of the preceding directions. These extra equations may be used to verify the final results, if desired. The comparisons best suited for the calculation are given in a table on a following page.

[2] If it is desired to refer the whole box of weights to the international standard, it is, of course, necessary to include a weight which has been standardized at Washington in the series, and thus to find the value of the international gram in terms of the centigram chosen as the temporary basis. The aliquot parts or multiples of this value are then used precisely in the manner indicated further on. For all ordinary purposes, however, this is wholly unnecessary; and one of the 10-gram pieces of the box is a more convenient standard.

[3] Nernst und Schoenfliess Math. Behand. der Naturwiss, p. 303 (1895).

Of course, if the weight is not heavy enough this correction carries a *minus* sign, and must be *subtracted* from the result of any weighing in which that weight is used; for the deficiency necessitates the addition of extra weight on the rider-arm, and hence the sum of the face-values of all the weights used is too large. Long experience has shown that the sign of the final correction is the most insidious cause of error in the whole process; for the beginner always thinks that if a given weight is too light, its correction should be *added*.

The table below presents all the data and results of a sample standardization, as well as all the calculation which need be written down by anyone possessing even a moderate ability to add figures mentally. In the first column the weights are named by their face-values, which are enclosed in parentheses in order to show that they do not signify true grams. In the second column are given the results of the mutual comparison of these weights copied from a note-book in which every detail of each weighing was recorded. The third column gives the actual values of the weights based upon the first centigram weight; these values are obtained by simply adding together the appropriate preceding values in the third column and the last minute fractional weight enumerated in the second column. The aliquot parts of the value for the 10-gram piece, which is now to be taken as the permanent standard, are recorded in the fourth column, while the corrections sought, obtained by simply subtracting the numbers in the fourth column from those in the third, are given in the last vertical row.

| Nominal values. | Data obtained by substitution method. | Preliminary values (actual). | Aliquot parts of 10.01768 (ideal). | Corrections in milligrams (actual minus ideal).[1] |
|---|---|---|---|---|
| | Grams. | Grams. | Grams. | |
| (0.01) = | Standard of comparison | Standard | 0.01002 | —0.02 |
| (0.01′) = | (0.01) + 0.00006 | 0.01006 | 0.01002 | +0.04 |
| (0.01″)= | (0.01′) — 0.00001 | 0.01005 | 0.01002 | +0.03 |

[1] Owing to neglected fractions the figures in the last column, when added together, are sometimes slightly discordant with those given in the second column. This is inevitable; of course such corrections should always be calculated to one decimal place beyond the figure which one wishes to have exact.

| Nominal values. | | | | Data obtained by substitution method. Grams. | Preliminary values (actual). Grams. | Aliquot parts of 10.01768 (ideal). Grams. | Corrections in milligrams (actual minus ideal).[1] |
|---|---|---|---|---|---|---|---|
| (0.02) | = | (0.01) | + (0.01′) | —0.00001 | 0.02005 | 0.02004 | +0.01 |
| (0.05) | = | (0.02) | + etc. | —0.00007 | 0.05009 | 0.05009 | ±0.00 |
| (0.1) | = | (0.05) | + etc. | —0.00006 | 0.10019 | 0.10018 | +0.01 |
| (0.1′) | = | (0.1) | | +0.00001 | 0.10020 | 0.10018 | +0.02 |
| (0.2) | = | (0.1) | + (0.1′) | —0.00004 | 0.20035 | 0.20035 | ±0.00 |
| (0.5) | = | (0.2) | + etc. | —0.00011 | 0.50088 | 0.50088 | ±0.00 |
| (1) | = | (0.5) | + etc. | —0.00004 | 1.00183 | 1.00177 | +0.06 |
| (1′) | = | | (1) | —0.00002 | 1.00181 | 1.00177 | +0.04 |
| (1″) | = | | (1) | —0.00006 | 1.00177 | 1.00177 | ±0.00 |
| (2) | = | (1′) | + (1″) | +0.00025 | 2.00383 | 2.00354 | +0.29 |
| (5) | = | (2) | + etc. | —0.00040 | 5.00884 | 5.00884 | ±0.00 |
| (10) | = | (5) | + etc. | —0.00040 | 10.01768 | 10.01768 | Standard. |
| | | etc. | | | etc. | etc. | etc. |

It is convenient to prepare from the individual corrections a card exhibiting at once the corrections corresponding to the usual combinations of weights from 1 to 99 centigrams and from 1 gram upwards. This card minimizes both the labor of applying the corrections and the danger of possible error in the process. It is hardly worth while to print here an example of such a card, but the method of application may be illustrated. The page of the note-book is ruled with two parallel vertical lines, which contain the two corrections found in the card. The upper correction corresponds in each case to the whole grams, and the lower to the fractional weights.

| | Observed weight. Grams. | Cor. mg. | Corrected weight. Grams. |
|---|---|---|---|
| Weight of crucible + substance | 19.3105 | +0.39<br>−0.01 | 19.3109 |
| " " " alone..... | 16.9916 | +0.06<br>+0.06 | 16.9917 |
| Weight of substance ..... | ..... | | 2.3192 |

Thus the increased accuracy is gained with very little sacrifice of time or mental labor. It is usually more convenient to adjust the rider by filing to exactly 12.0 (or 10.0) milligrams rather than to apply a correction for this also.

[1] See foot-note, p. 147.

The method of comparing the actual value with an ideal one is also a convenience in standardizing burettes by means of the Ostwald "calibrator." In the original description of this process it is assumed that the calibrator delivers exactly an integral number of cubic centimeters ;[1] but if only a few instruments are to be calibrated it is both troublesome and expensive to secure such a precise instrument. We have found it convenient to use a calibrator of any size, and to compare in parallel columns its multiples with the actual readings of the burette. The capacity of this calibrator is most conveniently obtained in the following manner. Suppose that as a mean of several comparisons it has been found that sixteen fillings of the calibrator correspond to 49.53 cc. on a given burette. Grease is the most serious foe to accuracy in this process. The burette is now refilled, and exactly this amount of pure water is run out into a weighed flask, with all the precautions which would be used in an actual titration. The weight of the water gives by appropriate calculation[2] the true volume of sixteen fillings of the calibrator. Suppose this was found to be 49.44 cc.; then the volume of the calibrator as it is actually used in a calibration must be $\frac{49.44}{16} = 3.090$ cc. The differences between the successive readings of the burette and the successive numbers 3.09, 6.18, 9.27, .... etc., give at once the errors of the graduation of the tube at these intervals. These differences or corrections may be plotted on a diagram in which the ordinates are volumes and the abscissas corrections. The correction to be applied for 50 cc. is obviously —0.09 cc. Here again the sign is somewhat perplexing to the inexperienced.

These simple methods have stood the test of years of use in our first course upon quantitative analysis, and their practicability under these circumstances shows that reasonable accuracy in weights and measures is within the easy reach of all.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
February 20, 1900.

[1] Ostwald: Handbook of Phys. Chem. Measurements (Walker), p. 87 (1894).
[2] This Journal, 21, 527 (1899).

# METHODS FOR THE DETECTION OF "PROCESS" OR "RENOVATED" BUTTER.

By W. H. Hess and R. E. Doolittle.

Received February 14, 1900.

"PROCESS" butter commonly called "renovated" butter is a product prepared about as follows: Unsalable dairy or creamery butter, bought at a low price in the spring and summer, is melted and the butter-fat drawn off. The curd originally present in the butter is rejected, thereby removing a large part of the rancidity if any be present. Milk is now added to this butter-fat and stirred in so as to be evenly mixed throughout, when the whole mass is cooled quickly, so as to prevent the separation of the "butter oil." This milk soon sours, the casein therein is coagulated, and thus there is provided an artificial curd which contains a percentage of nitrogen about the same as that of the curd of real dairy butter. The butter-fat of this renovated butter does not materially differ from ordinary butter-fat in any of its chemical properties.

It is evident, therefore, that for the detection of process butter, we must depend on the difference between the curd of genuine butter made from cream, and the artificial curd supplied in "process" butter by the addition of milk. There are proteids in milk which are insoluble in water, and therefore separate out and occur with the cream. The insolubility of these proteids was more fully brought out by S. W. Babcock in his work upon the proteids of cream (1888). These proteids, insoluble in water, pass into the butter and form the main part of the substance commonly known as the curd. It is a cohesive, gelatinous mass and notably non-granular. The curd of "process" butter, however, consists chiefly of coagulated casein. This is a flaky, granular, non-cohesive mass, and does not, therefore, resemble the proteids of cream in physical properties. The following method of analysis has proved satisfactory:

## TEST FOR BUTTER-FAT.

The purified fat is examined with the butyro-refractometer. At 25° C., the reading seldom varies from 51° in the case of "process" butter, and hence does not differ from butter-fat in

this respect. This reading is taken to assure the operator that the fat at hand is butter-fat and not a substitute, as oleomargarine. A determination of the volatile fat acids will serve as well.

### TESTS OF THE CURD.

After having proved that the fat is butter-fat, an examination of the curd is made. The first test that is made is one which depends on the cohesive properties of the curd of pure butter. If a portion of the butter sample, about 1 gram, is placed in a convenient container—a spoon answers the purpose admirably—and heated over a free flame, the mass will, in case the sample is pure butter, assume a foamy appearance, which is very striking. In case the sample is "process" butter, no foaming is produced, but the mass merely bumps and sputters like hot grease containing water. Oleomargarine behaves like "process" butter, but it has been excluded by previous tests.

### APPEARANCE OF THE CURD.

A sample of the butter is melted in a beaker, the fat is decanted, and the curd is well washed with ether to remove the remnant of fat. The curd is poured out on a clean glass plate in a thin layer and allowed to dry. A sample of genuine butter is treated likewise. The physical appearance is then quite distinctive especially when a magnifier of 3 to 6 diameters is used for the examination. The curd from the true butter will have an amorphous, non-granular appearance, while the curd from "process" butter has a very coarse, curdy appearance. The one is the proteid of cream, the other is the proteid of milk; the one is a gelatinous, ropy mass, the other is a granular, easily divided substance. Casein dissolves readily in acid or alkali; the curd of genuine butter dissolves only on prolonged treatment with these reagents.

### IDENTIFICATION OF THE SOURCE OF THE CURD.

A convenient sample of the butter, 25 to 100 grams, is placed in a beaker and melted at 45° to 50° C. (It is worthy of note that "process" butter will not yield a clear liquid fat at the end of half an hour or even twenty-four to forty-eight hours, while genuine dairy or creamery butter yields a clear supernatant liquid as soon as melted.) As much as possible of the fat is

decanted, and the remaining portions, composed of curd, water, salt, and the remnant of fat, are thrown upon a moistened filter and the water is allowed to drain through. This water carries the soluble proteids as well as salt. To this filtrate, a few drops of acetic acid are added and then the solution is brought to a boil. In case the filtrate is from the curd of pure butter, only a slight milkiness is produced (absence of albumins); but in case the filtrate is from the curd of "process" butter a flocculent, white precipitate of albumins is formed, a certain indication that the source of the curd is from milk. Other tests for the albumins may, of course, be used. If strong hydrochloric acid be added to the filtrate from the curd of "process" butter, a violet color is produced (Liebermann's test for albumin).

### QUANTITATIVE EXAMINATION OF THE CURD.

If the artificial curd of "process" butter has been derived from milk, then the ratio of the percentage of casein to the percentage of albumins should be the same as that ratio is in milk, or about 9 parts of casein to 1 part of albumins. The ratio in the curd of "process" butter sold on the market, as actually found, was 8.6 parts of casein to 1 part of albumins. The method of estimation is as follows: 50 grams of the butter are placed in a beaker and dissolved in ether to a clear solution. In case the sample is genuine butter, the curd is so finely divided that it remains in suspension in the ether and considerable time may be required for a clear solution. As much as possible of the ether solution of fat is decanted and the whole of the remainder transferred to a separatory funnel. The casein and water with the salt are then removed and the washing with ether repeated three or more times to remove all the fat from the curd. The casein is then filtered out, washed with water, and the nitrogen estimated by the Kjeldahl method. The filtrate from the curd is made slightly acid with acetic acid and then brought to a boil. The albumins are filtered out and estimated by the same method.

These tests serve to differentiate between genuine butter and "process" butter, as it is now found on the market.

LABORATORY OF THE MICHIGAN DAIRY
AND FOOD DEPARTMENT.

# CHEMICAL METHODS FOR ASCERTAINING THE LIME REQUIREMENT OF SOILS.

By H. J. WHEELER, B. L. HARTWELL, AND C. L. SARGENT.

Received February 20, 1900.

HAVING recognized the occurrence of an injurious degree of acidity in the upland soils of Rhode Island and other states, even upon steep hillsides, it became important to ascertain by chemical means if possible the relative lime requirement of different soils. If such could be done in a simple and effective way, then one would be in a position to recommend satisfactorily what amount of lime to use per acre without resort to field tests.

## TESTS BY BLUE LITMUS PAPER.

Perhaps the simplest, though nevertheless a very satisfactory test, is that made by bringing a piece of blue litmus paper in contact with the moistened soil and observing the intensity and rapidity of the reddening thus produced. Though unsatisfactory, in view of its not being a quantitative test, much valuable information regarding the amounts of lime which should probably be used, may thus be obtained, after some experience, by one who is a careful observer. Wahnschaffe[1] in speaking of this reaction says, "since the free carbonic acid of the soil reddens the paper, one must allow it to dry and observe whether or not the red color is still visible." Roscoe and Schorlemmer[2] state that "carbonic acid readily decomposes into water and carbon dioxide. In consequence of this, litmus paper which has been turned red in the aqueous acid, becomes blue on drying." They then immediately add that the reddening of litmus solution may be brought about by conducting into it carbon dioxide, but that upon heating the solution the carbon dioxide is expelled, and after boiling a few seconds the liquid again becomes blue. In Watts' Dictionary of Chemistry[3] it is stated that an "aqueous solution of $CO_2$ turns blue litmus paper wine-red ; the blue color returns on exposure to air." It seems probable that on account of the well-known reaction of litmus solution whereby, when reddened by carbon dioxide gas, it returns to a blue color, it has

[1] Anleitung zür wissenschaftlichen Bodenuntersuchungen, Berlin (1887), p. 56.

[2] "Treatise on Chemistry," I, New York (1888), p. 638.

[3] Vol. I, London (1890), p. 695.

been assumed that a similar reaction would necessarily take place when operating with litmus paper. This conclusion seems exceedingly probable since the writers have been unable to find references in the literature to any definite tests bearing upon this point. It is possible also that tests, if made, were carried out by operating with carbonic acid upon small sections of a piece of litmus paper, in which case, sufficient alkali might diffuse from the surrounding paper into the section acted upon, to neutralize the carbonic acid still remaining. That such a return of the blue color may result when the entire portion of the litmus paper is not subjected to treatment with acid, has been demonstrated by us upon commercial paper in the case of carbonic acid and of very dilute citric acid.

Owing to the action of the fingers upon blue litmus paper and the bleaching action of the sun, the test would be far simpler and more reliable in the hands of practical farmers if it were not necessary to wait for the paper to dry before drawing conclusions as to the probable needs of the soil. In view of the fact that some of the conditions prevailing when working with litmus paper are so different from those existing when employing the solution, it seemed probable that blue litmus paper, if entirely reddened by carbonic acid, and dried with the promptness that would ordinarily be expected, would not return to its original blue color. Dr. H. E. Stockbridge told one of us that he was under the impression that he once found this to be the case. In order to test this matter thoroughly, trials were made with ordinary commercial blue litmus paper and also with lots of paper prepared from solutions made according to Classen[1] and Sutton.[2] The carbonic acid was prepared by expelling the carbon dioxide from an aqueous solution of chemically pure sodium bicarbonate by simply boiling without the use of acid. A return condenser was employed and the carbon dioxide was washed in distilled water before its collection. Steam, generated from the distilled water which was used subsequently to dissolve the sodium bicarbonate, was first passed through the entire apparatus for some time and the distillate tested to insure the absence of

[1] Böckmann's "Chemisch-technische Untersuchungsmethoden", Vol. I, Berlin (1888), p. 97.

[2] The third method. Sutton's "Handbook of Volumetric Analysis", London (1882), p. 31.

volatile organic acids. Treated with carbonic acid prepared in this way all three lots of blue litmus paper were permanently reddened when dried naturally in the open air or in a room free from acids and ammonia. It is evident therefore that when dried naturally the carbon dioxide is not lost to any great extent or else the red, acid coloring-matter of the litmus is too firmly fixed upon the fiber of the paper, to permit of its reunion with the base, a change which would have resulted in the case of a solution, after the expulsion of the carbon dioxide. Coupling with these results the fact that so long as a liberal amount of calcium carbonate is present in a soil, the presence of carbonic acid tends to increase rather than lessen the tendency toward an alkaline reaction[1] (a point proved by us experimentally in the laboratory) it must be evident that the indication of acidity afforded by a piece of blue litmus paper is sufficient to show a deficiency of calcium carbonate or other basic ingredients in soils, without first allowing the paper to dry, as suggested by Wahnschaffe.

### TESTS BY EXTRACTION WITH AMMONIA.

Müntz[2] states that it is easy to distinguish whether or not a soil is acid, since if such is the case it imparts a black color to ammonium hydroxide when the two are brought in contact. He adds that in the case of soils which are not acid, the organic matter is in an insoluble combination with lime and consequently yields nothing to ammonium hydroxide. The same has been found by us to be the case with a sample of fertile adobe soil kindly forwarded by Professor Goss, from New Mexico. Similar observations have also been made on one Massachusetts and two Rhode Island soils where wood ashes or calcium carbonate in some form had been applied to the land with such frequency as to entirely overcome its acid reaction upon blue litmus paper. Snyder,[3] however, calls attention to a soil which he says contained 3.15 per cent. of lime (CaO) and 4.19 per cent. of carbon dioxide, and yet when treated with ammonium hydroxide for the determination of the so-called "free humic acid" yielded a dark brown extract amounting to from 0.3 to 0.4 of a

[1] Compare Detmer Die naturwissenschaftlichen Grundlagen d. allg. landw. Bodenkunde (1876), p. 451; also Stöckhardt, Jahrbuch für Agriculturchemie (1866), p. 10.

[2] Encyclopédie Chimique, 4, Pt. 4, p. 18.

[3] Bulletin No. 56, Chemical Division, United States Department of Agriculture, Washington, D. C., 1899.

per cent. This would tend to throw some doubt upon the reliability of the treatment with ammonium hydroxide as a means of arriving at the lime requirements of all soils, though it is not improbable that for soils of certain sections of the United States which are possessed of definite characteristics, the treatment may be of considerable value as was the case in the particular acid soils, for which Müntz employed the method. The details of the method as proposed by Müntz[1] are as follows: To 20 grams of powdered soil, add 50 cc. of concentrated ammonium hydroxide. Allow it to stand for from two to three days in a warm place. Agitate frequently and at the end of the period make the volume up to 1 liter. It is then shaken and allowed to subside for twenty-four hours. To 500 cc. of the liquid add sufficient hydrochloric acid to give a strong acid reaction in order to precipitate the humus, which carries with it some mineral matter. After the precipitate has subsided, decant the supernatant liquid, collect on a filter, dry and weigh in a weighing bottle, incinerate, deduct the ash, and the "free humic acids" are thus obtained by difference. In order to determine what influence, if any, the use of concentrated ammonium hydroxide might have upon the results compared with dilute solutions, a sample of upland soil was tested by the above method and yielded 1.00 per cent. Treated for the same time with the same amount of ammonium hydroxide previously diluted to 500 cc. (containing 1.13 per cent. of ammonia) it also yielded 1.00 per cent. The same soil treated for a like time with 500 cc. of the same solvent containing 2.4 per cent. of ammonia yielded 1.00 per cent. Employing sufficient concentrated ammonium hydroxide so that after diluting to 500 cc. it would have the same strength as in the last-mentioned instance, it yielded, treated for the same time, 1.03 per cent. It appears therefore that in the case of ordinary soils the strength of the solvent within reasonable limits is not an essential feature, and that the solution usually employed in total humus determinations may be used here with equal propriety.

### THE METHOD OF HOLLEMAN FOR DETERMINING THE LIME REQUIREMENTS OF STIFF CLAY SOILS.

Holleman[2] in searching for the cause of the occasional

[1] Encyclopédie Chimique, 4, Pt. 4, p. 182.
[2] Die landw. Versuchs-stationen 41 (1892), p. 38.

ineffectiveness of gas-lime upon certain stiff clays in Holland concluded that it might be due to the presence in them of considerable calcium carbonate. He thereupon made determinations of the lime removable by water and by water saturated with carbon dioxide. The water-soluble lime was determined as follows: Twenty grams of air-dried soil were digested with frequent shaking, at ordinary temperature, for forty-eight hours with 1 liter of distilled water. Five hundred grams of the filtrate to which a few drops of acetic acid had been added were evaporated, the residue taken up in water; and first a little acetic acid and then a measured quantity of $\frac{N}{10}$ solution of ammonium oxalate were added and the volume made up to 100 cc. After filtration, the excess of oxalic acid is estimated by titrating with a $\frac{N}{10}$ solution of potassium permanganate. For determining the lime soluble in carbonic acid 20 grams of air-dried soil are taken and sufficient distilled water added to make up 1 liter; it is then saturated with carbon dioxide and after twenty-four hours filtered and treated as described above. From the data obtained by Holleman, he concluded that where extraction with carbonic acid removed 0.15 per cent., or less, of calcium oxide, stiff clay soils would be benefited by liming.

In order to test the applicability of this method to the acid sandy and clayey loam soils of our State, two samples were selected, the first being from a farm in Warren, R. I., where, with the same manurial and other treatment, the yield of beets upon the unlimed plot was 272 pounds against 329 pounds upon the limed plot. The second soil was from Foster Center, R. I., where under the same conditions the yield of beets upon the unlimed plot had been 36.6 pounds and upon the limed one 143.4 pounds. In making the test of the soil from Warren, 80 grams of soil were employed, and in that from Foster Center, 40 grams. The soil was placed in each case in a flask to which 1 liter of distilled water, saturated with carbon dioxide, was added. The flask was agitated frequently and the treatment continued for forty hours. Four hundred cc. of the extract were evaporated to dryness, taken up in water and a little acetic acid, $\frac{N}{10}$ ammonium oxalate was added, and after filtration, the whole was made up to 200 cc. Aliquot parts of this solution were titrated with $\frac{N}{10}$ potassium permanganate, after acidulation with sulphuric acid. In

one instance the small amount of acetic acid was removed by evaporation to dryness before adding sulphuric acid and titrating without practically affecting the results. Allowing for the blank found, the amount of calcium oxide thus determined amounted in the Foster Center soil to 0.0360 per cent. In the case of the Warren soil, which was treated in the same manner, the amount of calcium oxide removed from the soil was found to be 0.0287.

The Warren soil extracted with distilled water, in a similar manner for forty-eight hours, yielded 0.0120 per cent. of calcium oxide.

From these tests it will be seen that the soil which was least benefited by lime, yielded less lime than the other. It is possible that the use of double the amount of soil in the last instance may have depressed the result somewhat as compared with the other, though it is not likely that the difference caused by this factor would, under the circumstances, have been readily appreciable. At all events the amount of lime removed in the highest case was only about one-fifth of that below which Holleman found lime useful on stiff clays.

It appears, therefore, in view of the marked degree of acidity of those of our soils which it seemed desirable to test as to their lime requirements, that this method is probably not of great value. It is regretted, nevertheless, that the pressure of routine work has prevented making further tests of the applicability of the method to our special needs, particularly with greater attention to maintaining the saturation of the carbonated water.

## THE METHOD OF TACKE FOR DETERMINING THE FREE HUMUS ACIDS IN THE PEAT (MOORBODEN) SOILS OF NORTH GERMANY.

Tacke[1] states that no method is known for determining quantitatively the acidity of soils, and calls attention to the desirability of possessing a satisfactorily exact method for the purpose. He discusses the difficulties in the way of determining the acidity by various ways which would naturally suggest themselves, and finally gives a method which yielded good results. It is impossible to give the method satisfactorily in

[1] *Chem. Ztg.*, No. 20, 1897, p. 174.

detail without reproducing the illustration of the apparatus which he employed. Essentially the method consists in expelling the carbon dioxide from calcium carbonate brought in contact with the soil at ordinary room temperature. Hydrogen is passed over the soil for some time in the apparatus, then finely divided calcium carbonate, shaken up with water, is introduced and allowed to act upon the soil for two and a half hours or longer as desired. The carbon dioxide disengaged is taken as a measure of the acidity of the soil, the amount being determined by passing it through a Pettenkofer tube containing $\frac{N}{5}$ or $\frac{N}{10}$ sodium hydroxide. The liquid is finally removed from the tube, taking care in regard to the absorption of carbon dioxide from the air, barium chloride then added and the solution titrated with $\frac{N}{5}$ or $\frac{N}{10}$ hydrochloric acid using phenolphthaleïn as an indicator with attention to the points brought out by the investigations by Küster[1] and by Lunge.[2] Determined in this way, using soil in its natural state, the amount of acid reckoned as carbonic acid, represented by 100 parts of dry material, amounted in the case of various peat soils to from 1.721 to 2.240 per cent. The method gives promise of much value for such soils as a guide to the amount of lime which they should receive. In April, 1895, experiments were begun by one of us for the purpose of ascertaining if the amount of carbon dioxide liberated from calcium carbonate upon heating it with upland acid soils in the presence of water, could be used as a guide to the amount of lime to apply to them. Owing to the pressure of routine matters, this work was several times taken up and then soon discontinued. Not having satisfactorily perfected a method at the time Tacke's results were published, it was decided to see if his method was applicable to our upland soils. Two unlimed soils were selected for the trial, the one from land where sodium nitrate had been applied for several years and the other from land where the manuring had been identical except that the same quantity of nitrogen had been applied in ammonium sulphate. The yields of most crops had been for several years far better upon the former than upon the latter plot of land.

[1] *Chem. Ztg. Repert.*, **29**, 282 (1896); *Ztschr. anorg. Chem.*, **13**, 127 pp. (1896).

[2] Bestimmung von Caustischen und Kohlensauren Alkalien, G. Lunge, *Ztschr. angew. Chem.*, **41** (1897).

The percentage of carbon dioxide obtained by treatment for three hours, calculated to dry soil, was 0.039 for the soil which had received sodium nitrate and 0.067 for the one which had received ammonium sulphate. In other words the results stood in the same relation as the yields. Taking into account the fact that the soils contained nearly 4 per cent. of humus and from 1.25 to 1.55 per cent. of humus immediately soluble in ammonium hydroxide, it is evident that the action of this class of soils upon calcium carbonate, at ordinary temperature, is far less vigorous than that of the peat soils tested by Tacke. The percentages obtained by this method are so small, and the element of error proportionately so great, that the indications are not particularly favorable to its use with soils of the character to which it was hoped the test would apply.

### DETERMINATION OF TOTAL HUMUS.

The determination of total humus could only be expected to throw light upon the lime requirement of soils where marked acidity of the soil exists, and while it might even then bear no relation to the benefit to be derived from liming, it was deemed of interest to ascertain by actual tests what relation, if any, would be found. Combined with the tests to determine the amount of humus soluble in ammonium hydroxide, without previous extraction of the soil with hydrochloric acid, it was also possible to learn if there appeared to be any relation between the gain from liming and the percentage of the total humus, which was directly soluble in ammonium hydroxide.

The method employed was essentially that of Grandeau as modified by Huston and McBride.[1] Twenty grams of soil were first extracted with hydrochloric acid as proposed by Hilgard[2] with the employment of an automatic washing apparatus, until no further reaction for lime was obtainable in the wash solution. After the removal of the acid by successive washings with distilled water, the material was extracted with ammonium hydroxide, aliquot portions of the extract evaporated to dryness, incinerated, the ash deducted and the humus thus obtained by difference. The relation between the results obtained and the data

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. I, 327, 328.
[2] *Ibid.*, p. 325.

secured in actual experiments with lime upon several soils will be discussed later.

### DETERMINATION OF THE AMOUNT OF LIME REMOVABLE BY HYDROCHLORIC ACID.

In soils containing some calcium carbonate, a number of methods have been proposed for arriving at their probable need of lime. Among others, Mondesir[1] gives a method by which he proposes to ascertain the active calcium carbonate in soils, since, as he says, soils may contain considerable of this substance, perhaps so surrounded by particles of clay that for practical purposes it is of little or no use, and nevertheless stand in need of lime. In our own soils which have been shown to contain practically no calcium carbonate, it must be evident that such methods can be of no avail. If the need of lime, in soils of the character under consideration, is determinable by the quantity of lime present, regardless of its form, then extraction with a strong mineral acid ought to serve as a fair basis for arriving at the lime requirement of the soil. Various methods of treatment, with different kinds, strengths, and volumes of acids have been proposed. For the purpose in hand the method[2] of the Association of Official Agricultural Chemists of the United States was followed, the digestion of the soil (10 grams) having been carried on for ten hours with 100 cc. hydrochloric acid (1.115 sp. gr.) at the temperature of boiling water with the employment of a return condenser. The data thus secured, with soils tested in a practical way with lime, in the field, are given later in tabular form in which connection they will be discussed.

### ACIDITY BY TITRATION.

If means could be devised for determining the relative acidity, or the lime requirements of soils by titration, the matter would be rendered extremely simple and the tests could be made in great numbers at small expense. Owing to the extreme insolubility of the acids, or acid compounds of the soil, the titration of a watery extract of the soil could not be expected to furnish any very valuable data. In order to obtain, if possible, results which might indicate in some measure the probable affinity for lime

[1] Annales de la Science Agron., 2, 270 (1887).

[2] Bull. 46, Div. of Chemistry, U. S. Dept. of Agriculture, pp. 39, 40.

(the substance which would usually be applied in the neutralization of soils), a study was made of the action of lime-water, the strength of the supernatant liquid, after contact with the soil for some time, being determined by titration. Air-dried soil was employed so as to eliminate any possible influence which might arise from drying at higher temperatures. Owing to the fact that these trials were only preliminary, and on account of the slight variation in the moisture of the soils examined which varied but little from 2.25 per cent., no correction has been applied to the results for the moisture contained in the soil itself. Ten grams of air-dried soil were brought in contact with 50 cc. of lime-water in a small flask. The flask was securely corked and occasionally agitated. At the end of about twenty hours the supernatant liquid was passed rapidly through a dry filter, an excess of hydrochloric acid of known strength (3 cc. neutralizing 36.1 cc. of the lime-water) added and the amount of unneutralized acid determined by titration with lime-water. In this way the volume of lime-water neutralized by 10 grams of the air-dried soil was indirectly determined. With the same soil more lime-water was required, without exception, where it had remained unlimed, than where lime had been applied. In the comparison of two unlimed soils manured alike excepting that one had received its nitrogen for several years in sodium nitrate and the other in ammonium sulphate, the differences in the amounts of lime-water neutralized were not always in harmony with, nor were they marked enough to accord at all with the experience obtained in tests of the soils made by plants themselves. In a comparison of limed and unlimed soils it was found that by employing a greater amount of lime-water (75 cc.) greater differences were obtained than by the use of but 50 cc. Possibly the use of even a somewhat greater amount would have given even better comparative results. Trials were also made, employing hydrochloric acid twenty times as dilute as that first tried. Coralline was used as an indicator, and though far from satisfactory in some respects, it was the only one tried which proved at all effective.

The preliminary trials not having indicated any particular general value of such a method, a trial of ammonium hydroxide was next made.

TITRATION TESTS BY MEANS OF AMMONIUM HYDROXIDE.

A number of preliminary tests gave indications that the use of ammonium hydroxide in place of lime-water, was capable of giving results more nearly in accord with those obtained by plant tests. The method finally used was as follows: Fifteen grams of air-dried soil were placed in a glass flask and 100 cc. of about $\frac{N}{10}$ ammonium hydroxide and 100 cc. of distilled water added. This was allowed to stand at the ordinary temperature of the laboratory for about forty-two hours, with frequent agitation during the earlier portion of the time. After it had finally been allowed to settle, a definite amount of the supernatant liquid was treated with hydrochloric acid (about $\frac{N}{2}$) at the rate of five cc. for each 20 cc. of the liquid, and made up to a given volume. After the precipitated humus had subsided, aliquot portions of the solution (50 cc.) were titrated with ammonium hydroxide, using coralline as an indicator. Since by this treatment some portion of the organic acids may be dissolved by the ammonia, the method cannot give an absolute idea of the acidity of a soil. On the other hand, a method which determines the humus immediately soluble in ammonium hydroxide before extraction with hydrochloric or other strong acid, gives no indication of the acidity represented by acid inorganic compounds. Possibly if the amount of humus soluble in ammonium hydroxide were determined, and likewise the amount of ammonia held at the same time in combination by the insoluble residue, the combined data might furnish a better guide than either one alone. Unfortunately the occasional opportunities available for conducting such investigations have not yet permitted a study of this question.

In order to ascertain what effect a variation in the strength and volume of the ammonium hydroxide and the volume of soil might have, a given[1] soil was tested in various ways.

(1) Twenty grams of soil were treated with 100 cc. of ammonium hydroxide diluted with a like quantity of water.

(2) Twenty grams of soil were treated with 50 cc. of ammonium hydroxide diluted with 150 cc. of water.

[1] Berthelot and André (*Ann. chim. phys.*, 7th Séries, 1, 286 (1894)) in operating upon organic residues from soils treated with hydrofluoric acid, state that the amount of potassium oxide held by the organic matter varied with the strength of the potassium hydroxide with which it was treated.

(3) Twenty grams of soil were treated with 200 cc. of ammonium hydroxide.

(4) Twenty grams of soil were treated with 150 cc. of ammonium hydroxide.

(5) Fifteen grams of soil were treated with 100 cc. of ammonium hydroxide.

The following were the amounts of ammonium hydroxide retained in combination by the soil calculated in each case to 10 grams of substance.

| | Ammonium hydroxide. cc. |
|---|---|
| (1) | 14.3 |
| (2) | 11.1 |
| (3) | 13.5 |
| (4) | 14.0 |
| (5) | 13.7 |

It will be seen from a careful examination of the data that they give some indication that only the weakest solution materially affected the results.

The trials of a number of Rhode Island soils by this method as described on page 170 are given in a subsequent table where the data may be compared with those obtained by other chemical methods and with the actual gains in yield of beets, obtained by the employment of lime.

METHOD FOR DETERMINING THE LIME REQUIREMENT OF SOILS BY COMPARING, UNDER IDENTICAL CONDITIONS, THE COLOR OF AN AMMONIUM HYDROXIDE EXTRACT OF SOILS OF UNKNOWN CHARACTER WITH ONE OF KNOWN CHARACTER.

The method employed was to treat in a warm room like amounts of soil with like volumes of ammonium hydroxide (containing about 2.4 per cent. of ammonia) for two days with occasional agitation. The small amount of water contained in the air-dried soil itself has been shown to exert no appreciable effect upon the result so that for approximate comparisons, drying a portion of the soil at a high temperature and making allowances for the water in the soil, is unnecessary. The colors of the solutions are finally compared and if darker than the standard, they are diluted with water to match it, or if lighter in color some of the standard solution prepared from the

soil of known character, is similarly diluted until it matches the one with which the comparison is being made. The amount of dilution in either case measures the excess or deficiency of color as compared with the standard. It was thought that certain weighable matters might be extracted by ammonium hydroxide from unhumified plant residues which might not color the solution to the same extent as the matter which is actually humified. In such a case, this method might perhaps give better indications than that as employed by Müntz (see page 155). The possible variation in color of the individual ingredients of the complex, which is classed as humus, may in some cases seriously interfere with the use of the method.

The rapidity with which a large number of comparative determinations can be made after the material has settled, is a strong point in its favor as compared with the method of Müntz. The results obtained by both methods may be compared below in connection with those obtained in actual plant tests upon limed and unlimed soil.

ATTEMPTS TO DETERMINE THE LIME REQUIREMENT OF SOILS BY MEASURING THE CARBON DIOXIDE EXPELLED UPON HEATING A GIVEN QUANTITY OF SOIL, IN THE PRESENCE OF WATER, WITH CALCIUM CARBONATE OR WITH SODIUM CARBONATE.

This work was begun in April 1895, at which time Tacke's method of treating peat soils at ordinary temperatures with calcium carbonate, had not been published. No notice of similar attempts to arrive at the lime requirement of soils having been found, the line of work was apparently wholly new and had to be conducted without the aid of any previous experience.

The first soil selected for this work was from the permanent experimental plot No. 23, which had been manured annually beginning with the year 1893, with the following commercial materials ; *viz.*, dissolved bone-black, potassium chloride and ammonium sulphate. The same arrangement was employed for the absorption of the carbon dioxide as is customary in ordinary determinations of carbon. As a preliminary trial 40 grams of soil, containing 24 per cent. of water capable of being driven off at 100° C., were placed in a Wolff flask and heated, in the

presence of water, with 4 grams of calcium carbonate. On account of the rapid evolution of carbon dioxide, the heating had to be conducted with the utmost care, as the boiling-point was approached, in order that the gas might be entirely absorbed.

A blank test with a definite amount of water and 80 grams of the soil (passed through a sieve containing holes $\frac{1}{25}$ of an inch in diameter) gave 0.0124 gram of carbon dioxide. A blank test with the water and 8 grams of calcium carbonate yielded 0.002 gram of carbon dioxide. Assuming that no carbon dioxide came from the calcium carbonate, 80 grams of the soil must have yielded upon heating in the manner described but (0.0124–0.002) 0.0104 gram of carbon dioxide.

Eighty grams of soil were heated with the same amount of water and calcium carbonate, and kept at the boiling-point until the evolution of gas seemed to have become practically constant and but very limited in amount. The carbon dioxide yielded, amounted to 0.338 gram. Assuming again that the entire blank from the water and calcium carbonate was due to the water and deducting therefore the blank of 0.0124 gram, it is seen that the amount of carbon dioxide found to have been liberated as a result of the action of the calcium carbonate upon the 80 grams of soil, was 0.3256 gram. Owing to rapid evolution of gas on approaching the boiling-point, which necessitated the frequent removal of the lamp, it was feared that some carbon dioxide must have passed through the entire apparatus.

A subsequent test with 40 grams of soil and 8 grams of calcium carbonate was then made. Deducting a blank of 0.0052 gram for the soil and 0.002 gram for the water and calcium carbonate, the amount of carbon dioxide expelled by the soil was found to be 0.1762 gram. This corresponds to 0.3524 gram for 80 grams of soil as compared with 0.3256 gram in the first test, but in the last test great care was exercised that no carbon dioxide should be lost.

A third test with 40 grams of soil and 4 grams of calcium carbonate yielded 0.178 gram of carbon dioxide. Deducting, as above, a blank of 0.0072, the amount of carbon dioxide found to have been liberated by the soil was equivalent to 0.3416 gram for 80 grams of soil.

In order to ascertain if differences between soils corresponding

to those shown by the growth of plants could be detected, a soil (from permanent Plot No. 27) was selected which had been manured the same as the other excepting that it had received its nitrogen in sodium nitrate instead of in ammonium sulphate. A blank test with 40 grams of soil and with the usual amount of water yielded 0.015 gram of carbon dioxide. A test with 40 grams of soil gave, after deduction of the blank just mentioned, 0.1402 gram of carbon dioxide or the equivalent of 0.2804 gram for 80 grams of soil, or much less than was shown by the soil first tested. This accorded with the results secured in plant tests and indicated much greater acidity where nitrogen in ammonium sulphate had been employed than where nitrogen in sodium nitrate was used, or where a basic instead of an acid residue had been left in the soil. In all of the tests thus far made, the operation was stopped after the chief evolution of gas was apparently over and when only a constant and very slight evolution was still noticeable.

To ascertain the effect of longer heating, 40 grams of soil and 4 grams of calcium carbonate were treated for a much longer time than heretofore. The amount of calcium oxide eliminated, allowing for the blank of 0.015 gram was equivalent for 80 grams of soil to 0.3126 gram as compared with 0.2804 gram where the period of heating was less prolonged. Another test was made under the same conditions, continuing the heating for about the same period as in the preceding instance. The net amount of carbon dioxide driven off, per 80 grams of soil, amounted to 0.322 gram. The same material brought to boiling once more and heated for some time yielded, per 80 grams of soil, 0.032 gram of additional carbon dioxide. Brought to boiling and heated for a third time the further loss for the same amount of soil was equivalent to 0.0256 gram. From these tests it appeared probable that beyond a certain point the attack upon the calcium carbonate became very limited or that a gradual oxidation or else a splitting up of the organic matter was taking place. To ascertain if this would go on at an appreciable rate at ordinary temperatures, a current of air was next passed for two and one-half hours over the material which had been thus successively heated. As a result it was found that no weighable amount of carbon dioxide had been eliminated. Further heating, as

before, resulted in a still further elimination of carbon dioxide and an increase in the weight of the absorption tubes. From this it was evident that there was apparently no reasonable time limit within which the elimination of carbon dioxide would be ended, and hence to obtain satisfactory comparative tests with different soils, the period of treatment, temperature, and other conditions must all be kept as uniform as possible. One apparent drawback to the method as it was used, was the necessity of conducting the heating so cautiously, and in consequence, for so long a time, in order that the carbon dioxide might all surely be absorbed, for by doing so the opportunity for the gradual breaking up of the organic matter was much increased. To overcome this objection, in a measure, the use of soda-lime was resorted to as an absorbent for carbon dioxide. By this means, less care was required to insure the absorption of the gas and the period of heating could be materially reduced. Nevertheless the method was still unsatisfactory, and in consequence, it was proposed to operate so as to subject the material to the action of heat a minimum length of time and either measure the volume of the carbon dioxide disengaged or to determine it indirectly by titration with the employment of barium hydroxide, or by estimating the amount of carbonate formed from it and so indirectly the carbon dioxide. Preliminary to this work it was thought wise to ascertain if possible the minimum time that it was necessary to heat the calcium carbonate and soil, in the presence of water, to insure that all of the humus had united with calcium oxide. It is well known that in many cases where soil contains naturally considerable quantities of lime and magnesia, ammonium hydroxide extracts practically no humus until the lime and magnesia have first been removed by acids. Such has been found to be the case in soil from New Mexico and with certain soils from Massachusetts and Rhode Island, which had been treated successively with calcium carbonate. The idea therefore suggested itself that by heating a number of soils with calcium carbonate and water for varying intervals of time, and subsequently testing the residues with ammonium hydroxide, it could be ascertained how long it was necessary to continue the heating in order to get practically all of the humus into an insoluble combination with lime. It was thought that this time

might be safely taken as the limit for continuing the heating and that the amount of carbon dioxide thus disengaged would serve as a suitable measure of the lime requirement of soils. It was also proposed to test the method with soils which do not react acid, in order that further light might be thrown upon the probable applicability of such a method to the purpose in hand. Unfortunately, routine work has prevented the further carrying on of this investigation. It is a question of too great scientific and practical interest to be laid aside at this point, and it is hoped that opportunity for further pursuit of the question will be afforded in the near future.

COMPARISON OF THE GAIN IN BEETS, RESULTING FROM THE USE OF LIME, WITH THE DETERMINATION OF THE LIME REQUIREMENT OF SOILS MADE BY VARIOUS CHEMICAL METHODS.

The following table shows the amounts of beets produced upon limed and unlimed soil in different sections of Rhode Island. Each plot was manured alike with commercial nitrate of soda, muriate of potash and dissolved bone-black. The table gives the percentage gain from liming, also the amount of humus immediately soluble in ammonium hydroxide, the percentage of "total" humus, the amount of calcium oxide removable by extracting with strong mineral acid, the number of milligrams of nitrogen in the ammonia held in combination by 10 grams of soil, the comparative dilution of the ammonium hydroxide extract of a soil of known character to give a degree of coloration corresponding to that exhibited by the extracts from the different soils tested, the amount of calcium oxide removable by carbonated water and the percentage of material in the respective soils which was so coarse as not to pass a sieve with openings $\frac{1}{25}$ of an inch in diameter. Only such material as passed circular openings of this size, was employed in the various tests.

The analytical data in the table were obtained with soil passing a sieve with hole $\frac{1}{25}$ of an inch in diameter. The results are calculated to dry soil.

| Locality. | Yield of table beets. | | Percentage gain in yield (of beets) from liming. | Total humus.[1] | Humus immediately soluble in ammonium hydroxide.[2] | Percentage of the total humus which was immediately soluble in ammonium hydroxide. | Milligrams of nitrogen in the ammonia retained from ammonium hydroxide by 10 grams of soil.[3] | Comparative amount of dilution in volume of the ammonium hydroxide extract of the Kingston soil to make it match in color similar extracts from the other soils.[4] | Lime (CaO) determined by the official method of the A. O. A. C.[5] | Lime (CaO) soluble in carbonated water.[6] | Soil materials too coarse to pass a sieve with holes ½ of an inch in diameter |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unlimed plot. | Limed plot. | | | | | | | | | |
| | Pounds. | Pounds. | | Per cent. | Per cent. | Per cent. | | | Per cent. | Per cent. | Per cent. |
| Warren ..... | 27.2 | 32.9 | 21.0 | 2.67 | 0.90 | 33.71 | 21.21 | 3.3 | 0.382 | 0.029 | 7.00 |
| Summit ..... | 47.4 | 92.9 | 96.0 | 1.73 | 0.84 | 48.55 | 19.61 | 4.0 | 0.386 | * | 22.30 |
| Jamestown .... | 75.8 | 152.7 | 101.5 | 0.85 | 0.53 | 62.35 | 10.41 | 5.0 | 0.261 | * | 1.15 |
| Harrisville .... | 151.5 | 207.3 | 102.8 | 1.46 | 0.42 | 28.77 | 14.09 | 6.6 | 0.429 | * | 11.75 |
| Foster Center . | 36.6 | 143.4 | 291.8 | 2.21 | 0.70 | 31.67 | 25.53 | 2.5 | 0.558 | 0.036 | 6.45 |
| Niantic ..... | 9.9 | 43.4 | 338.4 | 0.95 | 0.46 | 48.42 | 7.92 | 4.0 | 0.112 | * | 14.65 |
| So. Portsmouth | 26.0 | 153.0 | 488.5 | 2.63 | 0.99 | 37.64 | 27.16 | 2.5 | 0.348 | * | 7.25 |
| Hamilton ..... | 14.5 | 131.8 | 809.0 | 1.60 | 1.02 | 63.75 | 15.76 | 3.0 | 0.281 | * | 3.40 |
| Kingston Hill . | 6.6 | 161.4 | 2,345.5 | 5.15 | 1.99 | 38.64 | 36.09 | 0.0 | 0.412 | * | * |
| Slocumville .... | 1.0 | 101.8 | 10,080.0 | 5.08 | 1.41 | 27.76 | 43.77 | 0.3 | 0.553 | * | 1.10 |

* Not determined. [1] See method, p. 160. [2] See method, p. 163. [3] See method, p. 164. [4] See method, p. 164. [5] See method, p. 161. [6] See method, p. 157.

It will be seen that in the foregoing table the Warren soil which was least helped by lime, is placed at the top, the others being arranged in the order of the benefit noted, from top to bottom, with the Slocumville soil, representing a gain of 10,080 per cent. as a result of liming, placed at the foot of the list.

Comparing the percentages of material extracted immediately by treatment with ammonium hydroxide, with the gains from liming, it will be seen that there is no regular correspondence. The tests show a successive decrease in the first three soils while the crop increased. The Niantic soil shows a similar decrease. Of these soils, those at Niantic and Jamestown were exceedingly sandy, while those at Harrisville and Summit were quite gravelly. The result with the Warren soil was unexpectedly high. In the case of the balance of the "heavier" or more compact soils, a successive increase in humus immediately soluble in ammonium hydroxide was noticed, corresponding well, with the exception of the Slocumville soil, with the crop results. In fact this was the only method tried which indicated differences between the So. Portsmouth and Hamilton soils corresponding with those afforded by the crops. It will be noted that the Slocumville soil showed more benefit from liming than that at Kingston, though the latter gave a higher test by this method than the Slocumville soil. For the heavier classes of soils containing naturally considerable quantities of humus, this method gives much promise of usefulness. In the case of the more silicious soils containing but moderate amounts of humus, the method may perhaps indicate with considerable truthfulness the relative lime requirements within the particular class, but when it comes to comparisons of individuals of the one class with those of the other, it is possible that it fails to indicate the truth with sufficient accuracy on account of a considerable amount of the acidity being due more to inorganic, than to organic matter.

In support of this, it may be cited that many of our subsoils, which contain only minimum quantities of organic matter, are decidedly acid, indicating the presence of acid silicates, or other acid inorganic compounds. Mondesir[1] found that upon the destruction of all of the organic matter in a soil by means of "permanganate" at a temperature below 100° C., or by combus-

[1] *Compt. rend.*, **115**, 317, August (1892).

tion at dull red heat, and after subsequent treatment at ordinary temperature with very dilute hydrochloric or nitric acid, followed by complete removal of these by washing with distilled water and subsequent heating for several hours at from 160° to 170° C., the soil residue was still acid. It decomposed calcium carbonate to some extent at ordinary temperature, and still further upon heating with water to the boiling-point.

It is of interest to note that in the case of the Slocumville soil, where beets almost absolutely refuse to grow without the aid of lime, only 27.76 per cent. of the total humus was immediately soluble in ammonium hydroxide, and in the Kingston soil which stood second in its degree of benefit from liming, but 38.64 per cent. was soluble or much less than in many of the soils where lime proved far less beneficial. The percentage of the total humus which is thus dissolved is not then in any sense a true measure of the lime requirement, though the absolute amounts of humus thus dissolved, have seemed, particularly in our quite heavy soils containing considerable total humus, to correspond with considerable accuracy to the tests with beets.

Though there seems to be no reason to think that there would be any relation between the lime requirement of soils and their total humus on soils of widely divergent character, yet upon soils of analogous mineral origin, it seemed probable that some such relation might exist. The results obtained when plotted in a curve, show, with a few exceptions, the same general trend as those obtained by direct extraction with ammonium hydroxide. In the case of the Jamestown and Harrisville soils the total humus was higher in the former while the amount of humus immediately extracted, was greater in the latter. In the Hamilton soil, the total humus runs too low to accord with the crop test, while the amount of humus immediately soluble in ammonium hydroxide is greater in the case of that soil than in the one at So. Portsmouth, or in agreement with the results secured with beets. In regard to the Kingston and Slocumville soils, the total humus is slightly less in the latter than in the former, but the results come far nearer agreeing with the crop test, than those obtained by immediate extraction of the humus.

In the case of the determination of the lime (calcium oxide) removable from the soil by digestion with hydrochloric acid, the

results are of marked interest, since they show in the most striking manner that the data thus secured with our Rhode Island soils furnished no reliable guide to their lime requirements. As marked illustrations, it will be seen that the Foster Center soil which contained 0.558 per cent. of calcium oxide, or the greatest quantity of any of the soils examined, gave a gain in crop of 291.8 per cent. as compared with a gain from liming of only 21 per cent. in the Warren soil, which yielded only 0.382 per cent. of calcium oxide upon extraction with hydrochloric acid. Again the Slocumville soil showed by extraction with the mineral acid 0.553 per cent. of calcium oxide, or but 0.005 per cent. less than the Foster Center soil, and yet it was benefited by lime more than any other soil tested giving a gain from its use amounting to 10,080 per cent. The third highest content of calcium oxide as determined by extraction with hydrochloric acid was shown by the Kingston soil, which yielded 0.412 per cent., and yet the only soil which showed a greater benefit from liming was that at Slocumville where the percentage of calcium oxide was even much higher than at Kingston. These examples are sufficient to show that even if by this method of analysis considerable lime, even amounting to more than 0.5 per cent., is shown to be present, it may nevertheless be in such combinations that the soil will almost absolutely refuse to produce certain crops until subjected to liming or other alkaline treatment.

The number of milligrams of nitrogen represented by the ammonia retained by the soil, as determined by the method of titration, accords better with the crop results in the case of the Jamestown and Harrisville soils, than those obtained by immediate extraction with ammonium hydroxide. With the Hamilton soil, the result by the latter method agreed more closely with the crop tests, than those by the former, while in the case of the Kingston and Slocumville soils, the agreement with the crop results was more nearly perfect than those by any other method employed.

Only two tests were made by treatment of the soil with carbonated water. The soil which was the more in need of liming showed by this method a greater quantity of calcium oxide removable by the treatment than the other, or just the reverse of what should have been the case if the method were to

prove of value for the purpose in hand. This fact, together with some experience in the same line in connection with other soils, coupled with the small quantities of calcium oxide removable, gave little reason to hope that the method was applicable for ascertaining the true lime requirements of our acid Rhode Island soils.

The tests by means of the comparison of the color of the ammonium hydroxide extract in the case of the four upper soils in the table, *viz.*, those from Warren, Summit, Jamestown, and Harrisville indicate a gradation in the opposite direction from those with beets. The amount of total humus and the ammonia held by the soil as determined by the method of titration, agree, in the case of these soils, more nearly with the crop results. The results with the Foster Center and South Portsmouth soils, though not showing relative differences in the line of those exhibited by the crop, point, when compared with the first four soils in the series, in the same general way in relation to the soil requirements as the tests with beets. The results with the South Portsmouth and Hamilton soils fail to accord between themselves with the beet test, though the result with the latter soil, when compared with the first four of the series, points in the right general direction. Making a general comparison of the data secured with the Kingston and Slocumville soils with those in connection with the soils standing above them in the table, the tests point to the truth as concerns the needs of the soils. Between themselves the tests would indicate a slightly greater need of lime in the Kingston soil than in the Slocumville soil, or just the opposite of the actual experience.

In closing this consideration of these results, it should be stated that it was recognized at the outstart that unfavorable physical conditions might exert a very disturbing influence, and that in consequence a method which takes into account only chemical defects could not be expected to agree in all cases with the crop results. It was hoped, however, to combine physical analyses of the soil with the chemical, with the idea that possibly by a study of both, one might be helped very materially in arriving at a more correct judgment than by the use of either one singly. The resources at disposal have not as yet made it possible for these determinations to be made. There seemed no reason to

conclude that a physical analysis of the soils only, could come as near revealing their lime requirements as chemical tests, particularly as it had already been abundantly demonstrated[1] that the beneficial action of lime upon our soils is, in a large degree, due to its correcting their prevailing acidity.

## SUMMARY.

In consequence of the recognition of the acidity of many of the upland soils of Rhode Island and their consequent need of lime, it seemed desirable to find some chemical means for satisfactorily revealing their lime requirements, so as to avoid resorting to the slower and more expensive field experiments.

A number of methods have been tried, as follows:

(1) Moistening the soil with water, then bringing it in contact with blue litmus paper and noting with what rapidity and to what extent it reddens the paper as compared with some soil whose character is already well known. This method is highly effective in the hands of a close observer who has had much experience in testing soils of known character.

(2) Treatment of the soil with water to which a little ammonium hydroxide (ammonia water) has been added and noting whether, after settling, the liquid has assumed a dark brown or black appearance. This test applies only where the acidity is due in a considerable measure to acid organic substances. It may not apply in all sections of the country, as shown by Snyder, in Minnesota, but it has thus far proved a very useful and reliable test with Rhode Island and certain other New England and New York soils containing considerable quantities of humus. Gravimetrically applied this is the method of Müntz.

(3) The method employed by Holleman for determining the lime requirement of stiff clay soils in Holland, based upon the amount of lime (calcium oxide) removable by extracting with carbonated water. This method has given little promise of usefulness in testing our upland acid soils.

(4) The method of Tacke for determining the relative acidity of peat (moor) soils of North Germany based upon the amount of carbon dioxide which the acid ingredients of the soil can expel

[1] Eighth Annual Report, Rhode Island Agricultural Experiment Station, pp. 232-280 (1895); also Ninth Annual Report, pp. 294-318 (1896).

from calcium carbonate at ordinary temperatures in an atmosphere of hydrogen. This method has not seemed to be applicable to our acid upland soils.

(5) The determination of the total humus by a modification of the Grandeau method, which consists in removing the lime and magnesia from their combinations with the humus by treatment with dilute hydrochloric acid, and then dissolving the humus in ammonium hydroxide (ammonia water) and estimating the amount dissolved. In our granitic soils containing considerable quantities of humus, this method gives results standing in somewhat definite relation to the lime requirements.

(6) Determinations of the amount of lime (calcium oxide) which can be dissolved by weak hydrochloric acid by digestion at a high temperature for several hours (official method of the A. O. A. C.). This method furnishes no reliable basis for arriving at the lime requirement of our acid upland soils.

(7) Method by titration, based upon measuring the number of milligrams of nitrogen combined as ammonium salts and held by the soil when it is treated in a given way and for a given time with a very dilute solution of ammonium hydroxide.

The results by this method agree more closely with the crop tests than by any other method tried, though it is closely approximated to, by the gravimetric determination of the humus dissolved from the soil by extraction with ammonium hydroxide without the previous removal of the lime and magnesia.

(8) Method based upon the comparison of the color of the extract made from soils by treating directly with ammonia water, with the color of such an extract prepared from a like quantity of soil of known character. It seems probable that where the acidity is due largely to acid organic substances, this method may give fairly good results. The rapidity with which tests may be made by it is an important practical point in its favor as compared with the method as proposed by Müntz.

(9) Method based upon the amount of carbon dioxide expelled by a given amount of soil from calcium carbonate when the two are heated together at the boiling-point in the presence of water. This method gives promise of much value if the period of heating is made uniform and very brief, and if the carbon dioxide liberated is easily and accurately determined. Routine work

has thus far prevented further attempts to carry out a satisfactory study of this method including the perfection of its details.

LABORATORY OF THE RHODE ISLAND
AGRICULTURAL EXPERIMENT STATION.

## NEW BOOKS.

ANALYSIS OF WHITE PAINTS. A Collection of Notes on the Chemical Analysis of White and Tinted Paints. BY GEORGE H. ELLIS, B.Sc. Evanston, Ills.: The Technical Press. 8vo. pp. 57.

The notes under review were originally published in the *Paint, Oil and Drug Review*, of Chicago, and were prepared and edited by one who has had long practical experience in the technical examination of the products treated. They consist really of a collection of methods for analysis of paints and pigments long used by the author in his daily practice largely devoted to the products of the paint industry, and as the methods have been thoroughly tested and are described in the fullest detail they will be particularly useful to those chemists whose work has given them but limited practice with such products and methods.

With the methods of analysis in each case are presented results obtained by the author in the use of the methods, showing the average composition of the commercial product treated, and thus offers much useful information not easily found elsewhere. The book is commended to those whose duties lead them occasionally in the lines of work here treated and indeed to all needing guidance in the technical examination of pigments and paints.

WM. MCMURTRIE.

THE CHEMISTRY OF SOILS AND FERTILIZERS. BY HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station. Easton, Pa.: The Chemical Publishing Co. 1899. 12 mo. ix + 277 pp. Price $1.50.

We are told in the preface that this book was intended primarily to be used as a text-book in the author's classes. This fact explains the "experiments" and "review questions" which are given at the end of the book, as well as the condensed manner in which it is written.

It should answer admirably the purpose for which it was intended. The subject-matter is well chosen, well arranged, and clearly and concisely stated.

The style is as nearly popular as is possible with applied chemistry, and the book will be found of value even to agriculturists whose education has not included a course in chemistry.

W. D. BIGELOW.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR H. ELLIOTT, Ph.D. and GEORGE A. FERGUSON, Ph.B. Third edition, revised and enlarged. New York: Published by the Authors. 155 pp. Price, $1.50.

This manual contains a straightforward, carefully detailed procedure for the systematic qualitative examination of solutions or substances of moderate complexity. The analytical scheme is accompanied by a series of "solution tests" which the student is required to apply to each metal or acid radical and which include the reactions with certain general reagents, and with such special reagents as yield typical products. In connection with these tests a useful list of the important commercial compounds of each metal is given.

Certain of the schemes for the separation of the metals used in former editions have been altered or replaced by others (notably those of the copper and barium groups), and the procedure for the separation and detection of the acid radicals has been enlarged and improved. The book is liberally provided with tabulated statements of the methods of separation, and of the results of the "solution tests." The student can, indeed, hardly go astray within the field covered by the manual, so minute are its directions; yet, under the conditions imposed, the instructor will need to use much effort to encourage independence of thought and action on the part of the student.

The introduction of the "solution tests" is, perhaps, no more a proper subject for criticism in this manual than in many other similar works, but it may fairly be questioned whether so many of these isolated tests do not, by interrupting the study of the systematic plan of analysis, by confusing the beginner and lessening his interest, fail to serve a really useful purpose when the teaching of qualitative analysis is the central aim. To those teachers, however, who favor this method of presentation, the book will appeal strongly as a guide for beginners.

H. P. TALBOT.

PRACTICAL METHODS FOR DETERMINING MOLECULAR WEIGHTS. By HENRY BILTZ, Privatdocent at the University in Greifswald. Translated by HARRY C. JONES and STEPHEN H. KING. Easton, Pa.: The Chemical Publishing Company. 1899. 235 pp. Price, $2.00.

Previous to the appearance of the German edition of this work there was no satisfactory reference book on the determination of molecular weights, particularly by the vapor-density methods. Windisch's "Die Bestimmung des Moleculargewichts" was so voluminous and contained so many processes, with so much descriptive matter that it required an experienced hand to find just what was wanted, and therefore could not be used as a satisfactory laboratory guide. Fuchs's "Anleitung zur Moleculargewichts Bestimmung" was entirely satisfactory, but unfortunately was confined to the cryoscopic processes, thus leaving no satisfactory laboratory guide for the vapor-density methods.

This translation places in the hands of English-reading students a masterly summation of the practical methods for determining molecular weights by the vapor-density and the cryoscopic methods, with a careful criticism of the different procedures, and a comparison of the usefulness of one with the other. The author has been strongly under the influence of Victor Meyer, which gives an authoritative value to the Meyer displacement method and its various modifications. The separate methods are described with clearness and with that close attention to essential details which clearly shows the result of much experience. The critical discussion of the results obtained by the various methods is extremely valuable, especially those values obtained from substances which dissociate on heating, and those which suffer electrolytic dissociation in solution. The references to the literature are frequent and form a valuable part of the book.

The book contains chapters on the vapor-density methods of Meyer, Dumas, Gay-Lussac, and Hofmann, with the various modifications; and on the methods for determining molecular weights of substances in solution by the rise in boiling-point and the lowering of the freezing-point. The method of Nernst based on the principle of the lowering of the solubility is treated briefly. The process worked out by Traube and based on a comparison of the values from a determination of the molecular

volume and the theoretical value, is described, but is not recommended.

The translators have done their work satisfactorily. They have added a short chapter on the method and apparatus devised by Jones for the determination of molecular weights by the rise in boiling-point. HENRY FAY.

THE COST OF LIVING AS MODIFIED BY SANITARY SCIENCE. By ELLEN H. RICHARDS. 121 pp. New York: John Wiley & Sons. 1899.

This little book is a great disappointment to the student of sanitary science because of the misleading title which it bears. In no single instance has the author given us an idea whether the cost of living has been modified either favorably or unfavorably by sanitary science. She has shown that the cost of living has been increased by various causes which must, however, be classed as economic, social, and industrial.

The principal causes to which she attributes the increased cost of living are: The gross waste on the part of the housewife in reckless and useless expenditure for commodities which are unessential to health and happiness, and the improper utilization and even waste of the commodities purchased; also, the lack of proper interest in her duties, and want of appreciation of the importance of those duties on the part of the housewife. The factors which have brought about the foregoing conditions are mainly industrial, due to the removal of all manufacturing from the home to the factory, changing the occupation of the housewife almost altogether from that of a producer to that of a distributor. It will be seen that none of these causes are traceable to sanitary science.

The subject-matter presented is of marked interest and of the highest importance, and it is unfortunate therefore that it has been presented under a misleading title. Moreover it is to be regretted that the author has not adhered to the title given to the book because there is every reason to believe that the cost of living has been modified by sanitary science and a contribution embodying this information would be most valuable.

D. H. BERGEY.